

# PROCEEDINGS

OF

## THE PHYSICAL SOCIETY

### OF LONDON.

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MARCH 1893.

I. *Notes on the Construction of a Colour Map.*

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12

1. IN my paper on this subject, read before the Physical Society on April 8 last †, in discussing the method of plotting out the curve giving the mixtures of two spectrum colours, I stated that points in the curve lying in the abnormal or imaginary regions could not be determined by experiment. This I now find is a mistake.

Let  $S_1$  and  $S_2$  be spectrum colours, of which the mixtures are to be represented by points on the curve. The part of the curve lying in the imaginary and abnormal regions is obtained by *subtracting* light of one colour from light of the other colour, and equating the resulting colour to the mixture (if I may use the expression) obtained by *subtracting* white from some other spectrum colour  $S$ .

We have

$$n_1 S_1 - n_2 S_2 = S - xW.$$

This equation does not represent any possible physical experiment, but it may be transformed, without altering the value of any of the quantities, into

$$S + n_2 S_2 = n_1 S_1 + xW.$$

This last equation means :—Make a colour-patch of  $S$  and

\* Read October 28, 1892.

† Proc. Phys. Soc. vol. xi. p. 323.

$S_2$ , and a colour-patch of  $S_1$  and  $W$ , and vary the quantities of  $S_1$ ,  $S_2$ , and  $W$  until the two patches are similar in colour, and then measure the quantity of white. A line drawn to the left from the position of  $S$ , and proportional in length to the quantity of white, will define the position of the required point in the curve.

2. In the map the region on the right of the line of spectrum colours is occupied by all the colours obtained by mixing spectrum colours and white. I suggest that this should be called the Spectral Region. The equation for determining points on the mixture curves in the Spectral Region is

$$n_1S_1 + n_2S_2 = S + xW.$$

The region to the left of the abnormal and imaginary regions is occupied by colours complementary to those in the Spectral Region. I suggest that this should be called the Complementary Region. The equation for determining points on the mixture curves in the Complementary Region is

$$S + n_1S_1 + n_2S_2 = xW.$$

The equation for determining points on the mixture curves in the Imaginary and Abnormal Regions has just been shown to be (for one part of the curve)

$$S + n_2S_2 = n_1S_1 + xW,$$

and it is obvious that for the other part it will be

$$S + n_1S_1 = n_2S_2 + xW.$$

3. In defining a colour as compounded of a spectrum colour and white, we have to determine both quality and quantity of the white light.

A colour may be defined by three spectrum colours by means of the equation

$$n_1S_1 + n_2S_2 = n_3S_3 + xW,$$

or of the equation

$$n_1S_1 + n_2S_2 + n_3S_3 = xW.$$

The colour is that obtained when a patch formed in accordance with one side of the equation is made identical with a patch formed in accordance with the other. In this case

quantity of white need not be defined, but quality must be defined.

If a colour be defined by four spectrum colours the definition is independent of any convention as to the quality of white light. Let  $S_1, S_2, S_3, S_4$  be four spectrum colours whose wave-lengths are in order of magnitude, then the equation

$$n_1 S_1 + n_3 S_3 = n_2 S_2 + n_4 S_4$$

defines a certain colour, which can be obtained by making a patch of  $S_1$  and  $S_3$  identical in colour with one of  $S_2$  and  $S_4$ .

## II. *Experiments in Electric and Magnetic Fields, Constant and Varying.* By MESSRS. RIMINGTON and WYTHE SMITH.\*

[Plate I.]

THE object the authors have in bringing these phenomena before the Society is not to establish any new theory, nor to show imperfections in present theories, but to exhibit experiments which help the actions taking place in a dielectric under stress to be more easily grasped.

The experiments are divided into two sets :—

- (1) Performed in electric fields.
- (2) Performed in varying magnetic fields.

Although these two fields cannot exist separately, their effects are isolated.

### SET 1. *Constant Electric Field.*

A constant electric field was produced by two charged metal disks + and —, each of which was stuck on the outside of a glass plate (Plate I. fig. 1). The object of the glass plates was to prevent brush discharges between objects placed in the field and the plates.

Fig. 1,  $a, b$  represents a partially exhausted electrodeless tube, placed in the uniform electric field. In the position shown, the tube is at a uniform potential. Now let it rotate in the direction of the arrow ; the potential of  $a$  will fall and

\* Read November 25, 1892.



that of  $b$  rise until the P.D. between the ends is sufficient to break down the tube. There will then be a convection-current equalizing the potential, during the continuance of which the tube will glow. On rotating still further a similar action will take place.

The effect of these actions is to produce a double fan-shaped set of images, as shown in fig. 2. The number of images in the fan depends on the intensity of the field.

This phenomenon is intensified by constricting the middle part of the tube.

In designing the tubes for these experiments, care was taken to have the point where they were connected to the pump in such a position that there was no tendency for discharge to take place at these points when in use. The tubes used in this experiment are shown in fig. 3 ( $a$ ,  $b$ ,  $c$ , and  $d$ ). The stem was used to connect them to the whirling motor.

The surfaces of these tubes should be fairly clean and dry, and it is advisable with a new tube, or one left unused for some time, to excite it between the knobs of an influence-machine.

In the double fan-shaped set of images (see fig. 4,  $a$ ) one end will be seen to be brighter than the other, the current passing from the dull end to the bright end.

Not only is this effect visible with a straight tube, but on rotating an exhausted bulb in the field a stationary luminous region will be seen (see fig. 4,  $b$ ).

#### *Varying Electric Field.*

Instead of rotating the tube a similar effect is produced by varying the field in which the tube is placed.

The tube should be placed with its longer axis in the direction of the lines of force. The plates in this case may either be charged and discharged by an influence-machine and dischargers, the latter sparking, or by an induction-coil, with or without sparking.

When an induction-coil is used, very long tubes will glow when brought near.

#### SET 2. *Magnetic Field.*

The authors were of the opinion that, by taking advantage of the action of the Geissler tube, one might show Hertzian



phenomena to fairly large audiences. They therefore substituted a Geissler tube for the spark-gap in the resonator.

This was very successful with a Leyden-jar oscillator (fig. 5). The oscillator and resonator consisted of two similar small Leyden jars for capacity, and a single convolution of thick copper wire for the conductor-circuit. The Geissler tube was placed as a shunt to part of the conductor-circuit of the resonator (see fig. 5).

But although they designed special tubes, they were unable to get good results with the ordinary forms of Hertz oscillator and resonator.

They next made a resonator of the following form:—

Two metal plates, *a* and *b* (fig. 6), give capacity, and the wire self-induction. An electrodeless exhausted tube was placed as dielectric between the plates. When a fairly large Hertz oscillator was used, this tube glowed brightly, even when taken to considerable distances.

#### *Glow produced in varying Magnetic Fields.*

Instead of, as in the last set of experiments, having a secondary composed partly of a metallic conductor and partly of a vacuum-tube, the whole circuit may be composed of rarefied gas. It is evident that, in order to generate a current in such a circuit, a large induced E.M.F. would be required; this would necessitate either a very strong magnetic field, or one which changed very rapidly. The former was out of the question, the latter was obtained by taking advantage of the phenomenon of oscillatory discharge in the following manner:—

P (fig. 7), a primary consisting of a very few turns of gutta-percha covered wire, was placed in a Leyden-jar circuit, as shown. As a secondary an exhausted bulb, or annular tube, was placed near P.

On sparks passing at D, a bright ring of light appeared in the secondary.

In the actual experiments a metallic secondary, S, was also wound with P and exactly similar to it. On short-circuiting S, the induced current in this circuit will weaken the magnetic field so as to completely extinguish the Geissler secondary.

If S is connected to a third coil this coil will behave in a similar manner to P, with weaker effects; P and S in this case form a one to one transformer.

The wire of the coil P is itself luminous when S is open; short-circuiting S will stop this effect.

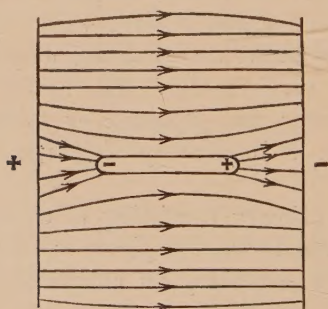
(Since the authors started their researches some of these latter experiments have been shown by Prof. Thomson.)

#### APPENDIX.

##### *Theory of a Vacuum-tube in a varying Electric Field.*

When an electrodeless vacuum-tube is placed axially between two plates, and a potential difference established between them, the tube forms part of the dielectric between the plates, and some of the lines of induction pass through the tube. Now a rarefied gas is a very weak dielectric, and readily gives way under the electric stress; a convection-current flowing through the tube (during which time the gas in the tube behaves as if it were a conductor)\*.

Fig. 8.



This results in the ends† of the tube becoming charged, or lines of induction from the plates terminate on the ends

\* Of course the tube will not conduct after the manner of a copper wire, but rather like a quantity of pith balls between two conducting plates.

† By the term "ends" is meant the *inside* surface of the glass at the ends of the tube.



of the tube, there being no lines in the tube itself (see fig. 8). The whole of the tube will also be at the same potential.

When the plates are discharged, the lines of induction passing from the plates to the ends of the tube will now pass through the tube; the rarefied gas will again break down under the electric stress, and a convection-current will pass through the tube until the charges at the ends neutralize each other.

If the change in the electric field take place rapidly enough, the convection-current will produce sufficient disturbance of the molecules to cause luminosity.

*Theory of a Vacuum-tube rotating in a constant Electric Field.*

Consider the tube in a constant field in position  $ab$  (fig. 9). There will be a  $-$  charge at " $a$ " and a  $+$  one at " $b$ ", and the tube will behave as a nonconductor. We shall in fact have conditions similar to those in fig. 10, where " $c$ " and

Fig. 9.

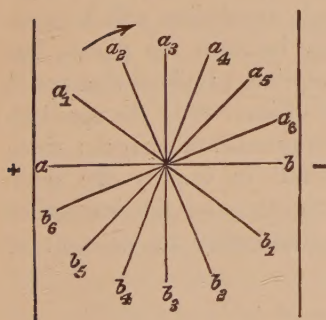
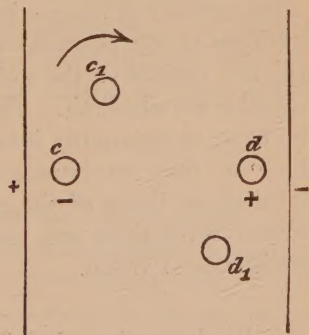


Fig. 10.



" $d$ " are two insulated conductors, which have been previously connected together by a conductor, and which correspond to the ends of the tube.

Imagine now " $c$ " and " $d$ " to be moved to positions  $c_1$  and  $d_1$ ; they will now be no longer at the same potential, and, if connected together, a current will flow from  $d_1$  to  $c_1$ , again equalizing their potentials,

The same will happen to the tube if it move during rotation from position  $ab$  to  $a_1b_1$ ; and, when the potential difference between its ends attains a sufficient magnitude, the dielectric of rarefied gas will break down, a convection-current flow from  $b_1$  to  $a_1$ , and the tube for the instant will behave like a conductor. During this instant of breaking down the tube will glow. After this the tube will behave like a nonconductor, the ends being at the same potential until the tube rotating moves into position  $a_2b_2$ , and, if the potential difference between  $a_2$  and  $a_1$  is equal to that between  $a$  and  $a_1$ , and the same for the  $b$ 's, the tube will glow for an instant at position  $a_2b_2$ .

In the same way it will glow in the positions  $a_3b_3$ ,  $a_4b_4$ , &c., if continuously rotated in the direction of the arrow. The points  $a_3a_4$  &c.,  $b_3b_4$  &c. are such that the potential difference between each consecutive two is approximately the same. As the glow takes place at the end of each alteration of the potential difference, it is obvious that the double fan-like set of images obtained will not be symmetrical with respect to the plates, but will be displaced in the direction of rotation by about one image.

The number of images in a single revolution will be proportional to the potential difference between the plates, but will not depend on the speed of rotation, provided that speed exceed a certain limit. The effect of increasing the speed is, however, to apparently increase the number of images; since those of one revolution do not fall in exactly the same positions as those of the preceding one, and the images of several revolutions are seen simultaneously on account of persistence of vision.

#### *Discharge through Coil surrounding exhausted Bulb.*

When a Leyden jar is discharged through a coil of wire, the varying magnetic induction due to the discharge-current will cause an E.M.F. to act in the dielectric inside and outside the ring in a series of concentric circles. Let  $r$  be the radius of the coil: consider a circular path in the dielectric of radius  $x$  less than  $r$ . If the magnetic induction passing through the coil were uniformly distributed, the number of lines passing



through the path  $x$  would be proportional to its area or to  $x^2$ , and the E.M.F. per unit of length along it to  $x^2$  divided by its circumference or to  $\frac{x^2}{x}$ , *i. e.* to  $x$ . Hence the electric stress along a circular path  $x$  in the dielectric is greater the larger  $x$ . Of course the actual distribution of the magnetic induction is not uniform, but increases as we pass from the centre to the circumference: this will of course make the electric stress increase more rapidly than  $x$ . When the dielectric is a rarefied gas it is not broken down until the electric stress exceeds a certain value: hence the discharge takes the form of a luminous ring in the outside of the bulb. By increasing the sparking-distance in discharging the Leyden jar the magnetic induction is increased, making the electric stress greater and broadening the ring.

The breadth of the ring also depends on the degree of exhaustion of the bulb, as the value of the electric stress requisite to break down the rarefied gas depends on the degree of rarefaction. In the case of an annular exhausted tube placed outside the coil the luminous ring will be nearest to the inner side of the tube: since when  $x$  is greater than  $r$ , the E.M.F. per unit of length is less the greater  $x$ , on account of the lines of magnetic induction outside the coil being in the opposite direction through the path  $x$  to those inside the coil.

#### DISCUSSION.

Mr. Swinburne thought some of the effects shown were not Hertzian, but merely cases of ordinary mutual induction. He enquired whether the vacuum-tubes would still glow if the Leyden jars were removed from the so-called resonating circuits. He was also of opinion that in the magnetic experiments the surfaces of the bulb, and not the enclosed gases, took the charges.

Mr. Watson asked if the authors had tried screening off the long waves by a wet cloth. If the effects still existed this would prove that they were Hertzian.

Prof. Ayrton remarked that the only cases where the materials of the bulbs, tubes, &c., did not influence the results

were those in which discharges were produced by varying magnetic fields.

Mr. E. T. Carter thought an induction-coil a more efficient machine for producing the glow in tubes than the alternator, &c., used by Mr. Tesla.

Prof. S. P. Thompson said he first noticed that sparks passed between pieces of metal in the vicinity of an induction-coil sparking into a condenser in 1876, when he was showing some experiments on telegraphic apparatus before the Society, but unfortunately he did not pursue the subject. Long before Mr. Tesla's investigations Dr. Bottomley had shown that exhausted tubes could be caused to glow, but it was not until Tesla produced such phenomena on a large scale that people recognized how much light could be got in that way.

Mr. Rimington, in replying to a question by Professor Thompson, said the notes heard when the glass plate approached the condenser were of very high pitch. The explanation, why in the experiments performed in varying magnetic fields the bright parts of the luminous discharges were near the wire, appeared to be that the E.M.F. was greatest in these places. Although he had not tried the experiment suggested by Mr. Swinburne of taking off the Leyden jar, he felt sure that doing so would stop the glow.

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### III. *The Diffusion of Light.* By W. E. SUMPNER, D.Sc.\*

11  
LITTLE information appears to have been published about the diffusing power of unpolished surfaces. The subject has been studied by optical measurements by Zöllner and others, chiefly for astronomical purposes; and the radiation from such surfaces has also been investigated with apparatus designed for measuring radiant heat. But the influence of such diffusion in increasing the illumination of rooms and open spaces, although well known, does not appear to be appreciated to the extent that its importance deserves; and a few numerical determinations of the coefficients of

\* Read December 9, 1892.



reflexion, absorption, and transmission of diffusing surfaces may prove of interest.

Terms in light are used vaguely, and it will not be deemed out of place to define those which will be here needed. By the *reflecting power* of a surface is meant the ratio of the amount of light reflected by it to the total amount of light incident upon it. The *illumination* of a surface is the amount of incident light per unit area of the surface. The unit *quantity of light* is the flux of radiation per second across a unit area of a sphere of unit radius at whose centre a unit light (of one candle) is placed. The amount of light radiated by a source of  $k$  candle-power, within a solid angle  $\Omega$ , is  $k\Omega$ , and the total quantity of light emitted by it is  $4\pi k$ . The *brightness* of a diffusing surface is its candle-power per unit area in the direction normal to the surface. The illumination produced at a point by a surface of brightness  $B$ , subtending a (small) solid angle  $\Omega$  at the point, is  $B\Omega$ , and if a surface, containing this point, have its normal inclined at an angle  $\phi$  to the axis of  $\Omega$ , the illumination of this second surface due to the first is  $B\Omega \cos \phi$ .

If  $B$  is the brightness of a surface rendered luminous by reflexion, if  $\eta$  is its (diffused) reflecting-power, and if  $I$  is the illumination of the surface, then

$$\pi B = \eta I. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This relation follows from the assumption of the law of cosines, viz. that the candle-power (per unit area) of a bright surface is  $B \cos \phi$  in a direction making an angle  $\phi$  with the normal. The right-hand member of (1) is by definition equal to the whole light reflected from unit area of the surface, and must be equal to the integral of  $B \cos \phi d\Omega$  for all directions on one side of the surface. The value of the integral is easily seen to be  $\pi B$ .

The brightness of a body, as just defined, is directly proportional to the illumination of the image of the body on the retina of the eye, and the word may thus be quite justly used in the ordinary physiological sense of the term. Similarly the law of cosines, just alluded to, is merely another way of expressing the fact that the sensation of the brightness of a diffusing surface is the same from whatever direction this

surface may be viewed. For the amount of light received by the eye, and concentrated on the image on the retina, is simply the product of the area of the pupil of the eye and the illumination at the surface of the eye due to the bright object. The former factor is constant for different directions of view, and the latter must vary as the solid angle subtended by the object at the eye, since the area of the image on the retina is a measure of this solid angle. The illumination at a point at which a surface of brightness  $B$  subtends a solid angle  $\Omega$  is not necessarily  $B\Omega$  for all inclinations of  $\Omega$  to the surface, unless the law of cosines is fulfilled; and, if this law is fulfilled, it follows that the illumination of the image of this surface on the retina of the eye is constant at all distances and inclinations. The eye is a good judge, and is indeed the only judge, of quick variations in brightness, and the cosine law is always applicable to diffusing surfaces, the appearance of which does not alter as the eye moves past them. Any divergence from this law is negligible so far as its influence on illumination is concerned.

If  $Q$  is the quantity of light radiated per second by the light-sources within a room, and if  $Q'$  is the total amount of light falling on the walls,

$$Q' = Q + \eta Q'. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For of the quantity  $Q'$ , a portion  $\eta Q'$  must be reflected, and the rest absorbed, and the rate at which light is absorbed by the walls must be equal to the rate at which it is produced. The average illumination  $I'$  of the walls of the room must hence be related to  $I$ , the illumination due to the direct action of the lights, by the equation

$$I' = \frac{1}{1-\eta} I. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus if  $\eta = .90$ ,  $I' = 10 I$ , and if  $\eta = .50$ ,  $I' = 2 I$ , so that the illumination due to the walls of the room may become far more important than that caused by the direct rays of the lights.

The truth of this relation may be also seen as follows:—The light  $Q$  falling on the walls is partially reflected, and a quantity  $\eta Q$  is sent back into the room. This light falls on the walls again and a portion  $\eta \times \eta Q$  is reflected a second



time. The total quantity of light  $Q'$  falling on the walls owing to successive reflexions is given by the equation\*

$$Q' = Q + \eta Q + \eta^2 Q + \dots = \frac{1}{1-\eta} Q.$$

Or, again, as the illumination  $I_p'$  of the walls at any point P is made up of a portion  $I_p$  due to the direct rays of the lights, together with a part caused by radiation from the walls, we have

$$I_p' = I_p + \int B \cos \phi \, d\Omega, \quad . \quad . \quad . \quad (4)$$

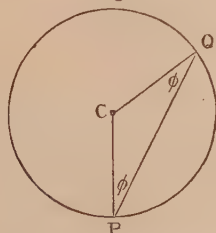
where B is the brightness of the walls, and  $\phi$  is the inclination of the solid angle  $d\Omega$  to the normal to the surface at the point P. Assuming that the brightness is the same all over the bounding surface of the room, the value of the integral is readily seen to be  $\pi B$ , and this, as already shown, is equal to  $\eta I'$ , where  $I'$  is the average illumination of the walls.

When the bounding surface of a room or enclosure consists of portions whose reflective powers are different, the average reflective power may be taken as

$$\eta_m = \frac{\eta_1 A_1 + \eta_2 A_2 + \&c. \dots}{A}, \quad . \quad . \quad . \quad (5)$$

where A is the total area of the bounding surface, of which a portion  $A_1$  has a reflective power equal to  $\eta_1$ , and a second portion  $A_2$  a reflective power  $\eta_2$ , &c. This relation is very

Fig. 1.



approximately true for ordinary rooms, and may be shown to be quite accurate for a spherical enclosure.

For let P and Q be any two points of a sphere of centre C

\* Since writing this paper I have discovered that this relation has been already pointed out by Mascart [see Palaz, *Traité de Photométrie Industrielle*, p. 268].

and radius  $r$  (fig. 1). Then  $PQ = 2r \cos \phi$ , where  $\phi$  is the angle which the chord makes with the radius through either P or Q. Also, with the same notation as before, we have

$$I_p' = I_p + \int B \cos \phi \frac{dA \cos \phi}{PQ^2},$$

where  $dA$  is an element of area at Q of brightness B, and subtending a solid angle  $dA \cos \phi / PQ^2$  at P. Now  $PQ^2 = 4r^2 \cos^2 \phi$  and  $\pi B = \eta I'$ , where  $I'$  is the illumination of the area  $dA$ : hence

$$I_p' = I_p + \frac{1}{4\pi r^2} \int I' \eta dA = I_p + \frac{1}{A} \int I' \eta dA, \quad (6)$$

A being the total area of the spherical surface. The integral is constant whatever the position of the point P, and whatever the character of the reflecting surface of the sphere. Thus if any complete [or if any portion of a] spherical surface be illuminated in *any* manner  $I_p$  by the direct rays of a combination of light sources, the actual illumination  $I_p'$  will exceed  $I_p$  by a constant amount all over the sphere, owing to the reflective action of the surface. Also, if the original distribution be uniform all over the sphere,  $I_p = I$ , a constant,  $I_p'$  will also be constant,  $= I'$ , and

$$I' = I + \frac{I'}{A} \int \eta dA = I + \eta_m I,$$

where

$$\eta_m = \frac{\sum \eta dA}{A}. \quad (7)$$

Taking as an average case for rooms a reflecting power of 70 per cent. for the ceiling, 40 per cent. for the walls, and 20 per cent. for the floor, the average value of  $\eta$  is a little over 40 per cent., and the increase of illumination by reflexion becomes as much as 70 per cent. If the walls and ceiling of a room be well whitewashed, the average reflecting power will not fall far short of 80 per cent.; and in such cases the illumination due to diffused reflexion is four times as important as that caused by the direct action of the lights in the room. A further great advantage, resulting from the use of good diffusing surfaces, arises from the fact that the

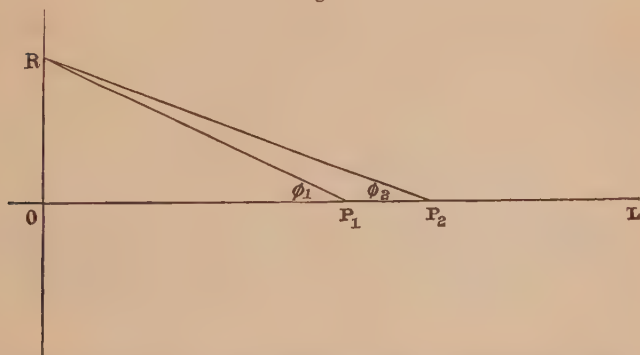
illumination they cause is, in most cases, very approximately constant all over the room, and does not cast shadows.

It is to be noted that when a reflecting surface is coloured, its average reflecting power does not properly represent the character of the increase of illumination caused by it. A room whose walls are covered with red paper whose average reflecting power is 40 per cent., may quite possibly have the red light in the room increased five times owing to the action of the walls. Suppose, for instance, that the reflective power of the paper for red light is 80 per cent., and for other kinds of light only 10 per cent., the average reflecting power will not exceed 40 per cent., yet the red light will be increased five times, while other kinds of light will not be increased to any perceptible extent.

*Measurements of Reflective Power.*

The surface, whose reflective power was required, was attached to a large screen of black velvet placed at one end O of a 3-metre photometer-bench OL (see fig. 2), so as to

Fig. 2.



be perpendicular to its length. Two lights were used, one being a Methven two-candle gas standard, placed at  $L$ , and the other a glow-lamp run generally at about 20 candle-power, placed at  $P_1$ . A Lummer-Brodhun photometer was slid along the bench to a point  $P_2$  at which the illumination due to reflexion from the surface  $OR$  was equal to that due to the Methven standard at  $L$ . At first the lamp  $P_1$  was



permanently situated a little to one side of the bench, and the rays from it in the direction of the photometer  $P_2$  were screened off. Subsequently the points  $P_1$  and  $P_2$  were made to coincide, the lamp being fixed to the same slider as the photometer and suitably screened from it and from the eyes of the observer. In some experiments the distance OL was kept fixed and the position of balance OP was determined for each surface tested. In other cases both OP and OL were varied.

Let:—

$A$  = area of diffusing surface on screen OR (centre at O).  
 $\Omega_1, \Omega_2$  = solid angles subtended by  $A$  at  $P_1, P_2$  respectively.

$x_1, x_2$  = distances  $OP_1, OP_2$  respectively.

$y$  = distance  $P_2L$ .

$K$  = candle-power of the glow-lamp at  $P_1$ .

$k$  = candle-power of Methven standard at  $L$ .

Then:—

The quantity of light falling on the area  $A$  is  $K\Omega_1$ ,

the average illumination of  $A$  is  $K\Omega_1/A$ ,

the average brightness is  $\eta K\Omega_1/\pi A$ , by (1),

the illumination at  $P_2$  is  $\eta K\Omega_1\Omega_2/\pi A$ ,

and also the illumination at  $P_2$  is  $k/y^2$ ;

whence

$$\eta = \frac{k}{K} \frac{\pi A}{\Omega_1\Omega_2 y^2} = \frac{k \pi x_1^2 x_2^2}{K A y^2}, \quad \dots \quad (8)$$

provided the dimensions of  $A$  are small compared with  $x_1$  or  $x_2$ . When this is not the case, the equation (8) is not sufficiently correct, and a more accurate formula may be obtained as follows, by taking note of the inclination of the rays to the surfaces.

The illumination of the surface at the point  $R$  due to the lamp at  $P_1$  can be easily shown to be  $K \cos^3 \phi_1 / x_1^2$ , where  $\phi_1$  is the angle between  $RP_1$  and OL, the line of centres of the bench. The brightness  $B$  of the surface at  $R$  is therefore  $\eta K \cos^3 \phi_1 / \pi x_1^2$  by equation (1). An element of area  $dA$  at  $R$  subtends at  $P_2$  a solid angle  $d\Omega_2$  equal to  $\cos^3 \phi_2 dA / x_2^2$ , and the illumination at  $P_2$  due to this element is  $B d\Omega_2 = \eta K \cos^3 \phi_1 \cos^3 \phi_2 dA / \pi x_1^2 x_2^2$  on any area placed perpendicular

to  $RP_2$ . As the photometer screen is perpendicular to the bench and not to  $RP_2$ , we must multiply this expression by  $\cos \phi_2$  to get the effective illumination due to the element  $dA$ . Finally we have for the total illumination the integral:—

$$I = \frac{\eta K}{\pi x_1^2 x_2^2} \int \cos^3 \phi_1 \cos^4 \phi_2 dA, \quad . \quad . \quad . \quad (9)$$

in which the angles  $\phi_1, \phi_2$  are related by the equation

$$x_1 \tan \phi_1 = x_2 \tan \phi_2.$$

When the area  $A$  is circular, with  $O$  as its centre, this integral reduces to

$$I = \frac{\eta K}{x_1^2} \int \cos^3 \phi_1 d \cdot \sin^2 \phi_2. \quad . \quad . \quad . \quad (10)$$

The value of this integral can be readily evaluated, but it does not lead to a convenient formula, and as it was found practically preferable to fix the lamp to the same slider as the photometer, and at the same distance from the screen  $OR$ , we may put

$$\phi_1 = \phi_2 = \phi,$$

$$x_1 = x_2 = x,$$

and (10) then reduces to

$$I = \eta \frac{K}{x^2} \frac{2}{5} [1 - \cos^5 \phi], \quad . \quad . \quad . \quad (11)$$

in which  $\phi$  is the semiangle of the cone with base  $A$  and height  $x$ .

This expression is rendered more convenient for purposes of calculation by taking advantage of the fact that  $A/\pi x^2$ , or  $\tan^2 \phi$ , is a small quantity. By neglecting  $\tan^6 \phi$  compared with unity we obtain

$$\frac{2}{5} [1 - \cos^5 \phi] = \frac{1}{X},$$

where

$$X = \frac{\pi x^2}{A} + 1.75 + .43 \frac{A}{\pi x^2}; \quad . \quad . \quad . \quad (12)$$

and in most cases it will be found that the third term in this expression is negligibly small compared with the sum of the other two.

The value of  $I$  found in (11) may be equated to  $k/y^2$  when

the photometer is in the position of balance, and on doing so, we find for  $\eta$  the value

$$\eta = \frac{k}{K} \frac{x^2}{y^2} X, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which reduces to (8) when  $x$  is large.

This equation was used for the great majority of the reflexion tests. With feebly diffusing surfaces such as black cloth, the distance  $x$  had to be so much reduced that the area  $A$  subtended a greater angle at the photometer-screen than the aperture of the photometer itself. In such cases the angle  $\phi$  in (11) was calculated from the solid angle subtended by the aperture of the photometer at the centre of the photometer-screen. With diffusing surfaces which appeared to shine slightly under the action of light, the effect of regular reflexion had to be separated from that of diffused reflexion, by experiments made with the same surface for different values of  $x$ . In such cases, which will be alluded to subsequently, the true reflecting-power is not given by formula (13). The areas  $A$  of the reflecting surfaces used in the experiments were never circular, as assumed in the above proof, but as they were always approximately square, with the central portion at  $O$  (fig. 2), any error in (12) and (13) arising in this way must be quite negligible. The ratio  $k/K$  of the two lights was frequently tested in the course of the experiments and was found very constant during every set of tests.

The results obtained are given in the accompanying table. In the majority of cases the numbers given are approximate only, as there seemed no object in aiming at great accuracy. The first four surfaces referred to in the table, viz., thick white blotting-paper, white (rough) cartridge-paper, tracing-paper, and tracing-cloth, were, however, carefully tested, and the numbers obtained represent the mean of many observations.

Zöllner found white surfaces to reflect from 70 to 78 per cent. of the light incident upon them. The numbers given at the head of Table I. are slightly higher. They, however, agree very well with results which have been published with regard to the diffuse reflexion of radiant heat,



since 82 per cent. is generally given as the reflective power of white substances\*.

TABLE I.—Reflecting-Powers.

	per cent.		per cent.
White blotting-paper .....	82	Plane deal (clean) .....	40 to 50
White cartridge-paper .....	80	„ (dirty) .....	20
Tracing-cloth .....	35	Yellow cardboard .....	30
Tracing-paper .....	22	Parchment (one thickness) ...	22
Ordinary foolscap .....	70	„ (two thicknesses) ...	35
Newspapers .....	50 to 70	Yellow painted wall (dirty) ...	20
Tissue-paper (one thickness) ...	40	„ „ „ (clean) ...	40
„ (two thicknesses) ...	55	Black cloth.....	1·2
Yellow wall-paper .....	40	Black velvet .....	0·4
Blue paper .....	25		
Dark brown paper .....	13		
Deep chocolate paper .....	4		

The degree of consistency of the results may be judged as follows :—In a series of 10 determinations of the reflective power of white blotting-paper, made with values of  $x$  (see fig. 2), varying from 40 cm. to 82 cm., the mean reflecting-power was found to be 82·4 per cent., and the average error of a single determination from the mean was 1·4. With surfaces of lower reflecting-power (such as tracing-cloth) the numbers obtained in successive experiments were more consistent. The value of  $\eta$  for white blotting-paper was checked by comparing it directly with that of a piece of common mirror. The Methven standard at L (see fig. 2) was replaced by the mirror, arranged so as to reflect the light from the glow-lamp along the line of the bench. The reflective power of the white blotting-paper placed on the screen OR was found to be 98·5 per cent. of that of the mirror. The value of  $\eta$  for the mirror, for normal rays, was separately determined and found to be 82 per cent., and hence  $\eta$  for the blotting-paper comes out as 80·8 per cent.

Several of the numbers in the above table were confirmed by comparative measurements, using white paper as a standard reflector, the Methven standard at L (fig. 2) being replaced by a surface of white paper exposed to the rays of the glow-lamp at P. The reflective power of one of the walls tested

\* See Jamin et Bouty, Tome Troisième, p. 149. Results by MM. Goddard, De la Provostaye et Desains.

was measured in diffuse daylight by exposing the aperture of a photometer to the radiation of the wall, and balancing the illumination against that of a standard candle. The part of the wall affecting the photometer was then covered with a sheet of white blotting-paper, and the ratio of the two illuminations at once gave the ratio of the reflecting-powers.

### *Measurement of Absorption.*

The absorbing-powers of some of the preceding substances were determined by measuring the candle-power of the light from a glow-lamp, first when this was uncovered, and afterwards when it was surrounded with a cylinder of the paper under test. The cylinders were short, being just longer than the height of the lamp, and were closed at top and bottom with caps of the same paper, so that the lamp was completely enveloped by the paper tested. The ratio of the diminution of candle-power to the original candle-power gave the *apparent* absorption of the paper. If the candle-power in some particular case was found to diminish 30 per cent., it would have been erroneous to conclude that the envelope absorbed as much as 30 per cent. of the light incident upon it, or that 70 per cent. was transmitted. If the reflecting, absorbing, and transmitting powers of a material be respectively denoted by  $\eta$ ,  $a$ , and  $\tau$ , there must exist between these quantities the relation

$$\eta + a + \tau = 1.$$

Also if  $Q$  be the quantity of light given out per second by the light-source within the envelope, the quantity of light incident per second upon the surface of the envelope will, owing to internal reflexion, be increased to  $Q'$ , where

$$Q'(1 - \eta) = Q;$$

the quantities of light absorbed and transmitted will respectively be

$$aQ' \text{ and } \tau Q',$$

and the ratios these quantities bear to  $Q$  will similarly be

$$\frac{a}{1 - \eta} \text{ and } \frac{\tau}{1 - \eta};$$

the sum of course being unity.

If the light-source can be assumed to radiate equally in all directions, the ratio of its candle-power, after putting on the envelope, to the original candle-power will not be  $\tau$  but  $\tau/(1-\eta)$ . The influence of internal reflexion is to increase *both* the absorption and the transmission, and unless it is taken into account large errors may be made in estimating the coefficients. A very simple way of showing the effect of internal reflexion consists in surrounding a glow-lamp with a white paper cylinder, open at the top, and adjusting a photometer screen till the illumination caused by it is balanced against that of some standard source of light. If now a piece of white paper be placed on the top of the cylinder, so as to shut in the vertical rays of the lamp, the candle-power in the horizontal direction will be found to increase considerably. In some of the tests, in order to avoid error caused by non-uniform radiation of the lamp, this was first surrounded with an envelope of tracing-cloth, or blotting-paper, and the combination used as the light-source. If  $k_0$  be its candle-power in this condition, and if  $k_1$  be the observed candle-power after completely surrounding it with an envelope of the substance to be tested, the apparent absorption of this material is

$$\frac{k_0 - k_1}{k_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and the true absorption coefficient  $\alpha$  is given by

$$\alpha = (1 - \eta) \frac{k_0 - k_1}{k_0}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where  $\eta$  is the previously found reflexion coefficient.

When an inner envelope is used to produce a light which radiates equally well in all directions, it is necessary for the outer envelope to be large compared with it, since otherwise the formula for the increase of illumination due to internal reflexion cannot be applied.

The following table gives the values of the absorbing coefficients, expressed as percentages, for the four substances at the head of Table I., from which the corresponding values of  $\eta$  used in applying (15) have been taken.



TABLE II.

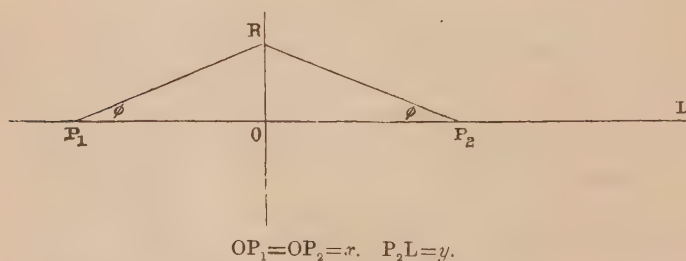
	Apparent Absorption.	Real Absorption.
White Blotting-paper .....	77 per cent.	13·8 per cent.
White Cartridge-paper .....	61    ,,	12·2    ,,
Tracing-cloth .....	23    ,,	15·0    ,,
Tracing-paper .....	9     ,,	7·0     ,,

Three large glass globes, made for arc-lamps, were also tested. As the reflective powers of the globes could not easily be found, only the apparent absorption was measured. One globe was of opal glass (almost transparent), and the ratio of apparent absorption was 15 per cent. A second globe was of ground glass and absorbed 42 per cent. The remaining one was of opal glass, too opaque to allow any bright object placed within it to be distinguished. This absorbed 39 per cent.

*Measurements of Transmitting-Power.*

The amount of light transmitted through the surfaces above mentioned was measured in a very similar manner to that in which their reflective powers were determined; the only difference being that the glow-lamp at  $P_1$  (see fig. 2) was moved to the opposite side of the surface as in fig. 3.

Fig. 3.



OR represents the screen of paper, pinned on a wooden frame, and placed perpendicular to the optical bench  $P_1L$ . The

glow-lamp was at  $P_1$ , the photometer at  $P_2$ , and the Methven standard at  $L$ . The distances  $OP_1$ ,  $OP_2$  were arranged to be equal, and balance obtained by moving  $L$  along the bench. On referring to equations (8) to (13) and the arguments used in establishing them, it will be seen that they are all applicable to the case now considered if only we substitute  $\tau$ , the transmitting-power, for  $\eta$ .

When, however, tests were made with the paper surfaces already referred to, it was soon found that the numbers calculated from expression (13),

$$\frac{k}{K} \frac{x^2}{y^2} X = Y, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

were not constant for the same substance. They differed from each other far more than could be accounted for by errors of experiment; thus, the values found for  $\tau$  by this formula were too high, and frequently exceeded 100 per cent. For any given surface the values were found to increase progressively with the value of  $x$  used in the tests. The reason for this is easily seen when it is remembered that equations (8) to (13) are only true on the assumption that the surfaces considered are purely diffusive, and do not alter in appearance as the eye changes its point of view. When light is transmitted through a semitransparent substance such as tracing-paper, or tracing-cloth, the brightest part of the surface is always on the line joining the eye to the light, and visibly moves over the surface as the point of view is changed. The easiest way to represent these facts is to assume that, of the light transmitted, a portion  $\tau_1$  passes through without change of direction, and that the rest  $\tau_2$  is diffused in accordance with the cosine law. The case is analogous with a reflecting surface such as white enamelled iron, which reflects a portion  $\eta_1$  of the incident light in accordance with the regular law of reflexion, and diffuses another portion  $\eta_2$  according to the law of cosines. On referring to equations (8) to (11) it will be noticed that they are still true for the illumination due to diffusion if we substitute for  $\eta$  either  $\tau_2$  or  $\eta_2$  (according as we are considering transmission (fig. 3) or reflexion (fig. 2) respectively). The additional illumination at the photometer

due to regular, *i. e.* direct, transmission (transparency) is

$$\tau_1 \frac{K}{(2x)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and a similar expression holds for regular reflexion if we substitute  $\eta_1$  for  $\tau_1$ .

The whole illumination must, as before, be equal to  $k/y^2$ , and by (11), (12), and (17) we have

$$\tau_2 \frac{K}{x^2 X} + \tau_1 \frac{K}{4x^2} = \frac{k}{y^2}, \quad . \quad . \quad . \quad . \quad . \quad (18)$$

whence the value of  $Y$  in (16) is equal to

$$Y = \tau_2 + \frac{\tau_1}{4} X; \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and a similar expression holds for reflexion if we replace  $\tau_1$  and  $\tau_2$  by  $\eta_1$  and  $\eta_2$  respectively. The true values for the transmitting and reflecting coefficients are

$$\left. \begin{aligned} \tau &= \tau_1 + \tau_2, \\ \eta &= \eta_1 + \eta_2, \end{aligned} \right\}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and the reason the values found for  $Y$  were too high, and became greater and greater as  $x$  increased, was simply that the values used for  $X$  (see 12) were always greater than 4, and increased rapidly with  $x$ .

By plotting the numbers found for  $Y$  with the corresponding values of  $X$ , a straight line is obtained from which the values represented by the symbols in (20) can all be determined. The straightness of these lines, and the verification of the fundamental formula

$$\eta + \alpha + \tau = 1,$$

affords a good criterion of the extent to which the principles and the formulæ, referred to in this paper, can be relied upon.

The following Tables III., IV., and V. contain the results of three sets of tests on the transmitting-power of blotting-paper and tracing-cloth, and on the reflecting-power of tracing-cloth. The values of  $Y_{\text{obs.}}$  are calculated with the aid of (12) and (16) from the observed values of  $x$  and  $y$ . All the dimensions are given in centimetre-units. In the accompanying sheet of curves the values of  $Y_{\text{obs.}}$  are plotted as



ordinates, with the corresponding values of  $X$  as abscissæ. From the straight line most nearly representing the connexion between the points the values of  $Y_{\text{calc.}}$  have been obtained, and are given in the tables. From this straight line also the true value of the transmitting (or reflective) power can be found by finding the value of the ordinate when  $X=4$ . The intercept on the axis of  $Y$  shows the portion of the light which is diffused.

TABLE III.—Transmitting-Power of Blotting-paper.

$$A=980. \quad K=26. \quad k=2. \quad \tau=9.2. \quad Y_{\text{calc.}}=6.50+2.7 X/4.$$

$x$ .....	60	50	40	45	55	60
$y$ .....	154	120	88.4	104.6	137	154
$X$ .....	13.6	9.8	7.0	8.25	11.40	13.6
$Y_{\text{obs.}}$ .....	15.5	13.2	11.2	12.0	14.4	15.5
$Y_{\text{calc.}}$ .....	15.7	13.1	11.2	12.1	14.2	15.7

TABLE IV.—Transmitting-Power of Tracing-cloth.

$$A=980. \quad K=23.1. \quad k=2. \quad \tau=54.4. \quad Y_{\text{calc.}}=41.0+13.4 X/4.$$

$x$ .....	40	50	60	70	80	75	65	55	45
$y$ .....	39.2	53.5	70.1	89.4	105.6	95.8	77.7	61	46.1
$X$ .....	6.98	9.80	13.6	17.4	22.30	19.4	15.4	11.2	8.25
$Y_{\text{obs.}}$ ...	63.5	74.3	86.1	97.0	116	107	91.8	81.7	69.3
$Y_{\text{calc.}}$ ...	64.4	73.7	85.6	99.2	115.8	106	94.0	78.5	68.7

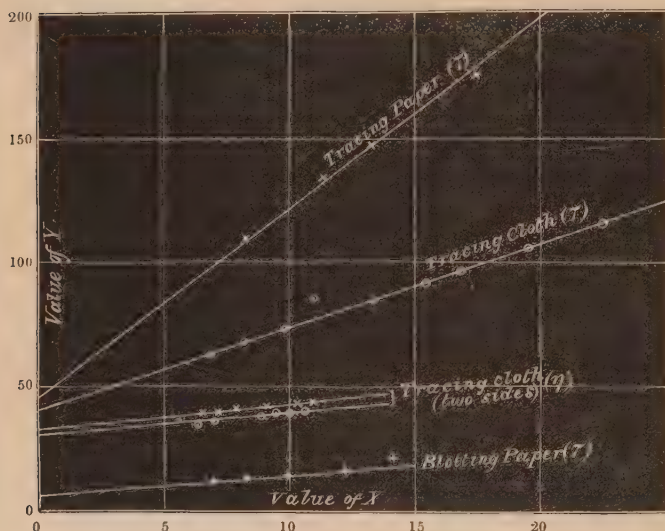
TABLE V.—Reflecting-Power of Tracing-cloth (shiny side).

$$A=1300. \quad K=12. \quad k=2. \quad \eta=35.7. \quad Y_{\text{calc.}}=30.9+4.8 X/4.$$

$x$ .....	50	55	62.3	59.8	47.5	44.5
$y$ .....	90	104.4	127.7	120.2	82.5	75.5
$X$ .....	7.82	9.10	11.13	10.45	7.22	6.55
$Y_{\text{obs.}}$ .....	40.4	41.8	44.1	43.2	39.6	38.6
$Y_{\text{calc.}}$ .....	40.3	41.8	44.2	43.4	39.6	38.7

Several sets of tests were taken. Some of these are represented by the sheet of curves shown in fig. 4.  $Y$  is the percentage of the incident light which the surface *apparently*

Fig. 4.



reflects or transmits, assuming that it is all diffused, and is calculated from equation (16). The true values of the coefficients are obtained from the curves by applying equations (19) and (20). The numerical details of the observations are of no special interest, and the essential results may be summarized as follows:—

TABLE VI.—Reflective Powers.

	Regular. $\eta_1$ .	Diffused. $\eta_2$ .	Total. $\eta$ .
Blotting-paper .....	0 per cent.	82 per cent.	82 per cent.
Cartridge-paper .....	0 "	80 "	80 "
Tracing-cloth (shiny side) ...	4.8 "	30.9 "	35.7 "
" " (rough side)...	2.7 "	31.6 "	34.3 "
Tracing-paper .....	2.2 "	19.8 "	22.0 "

TABLE VII.—Transmissive Powers.

	Direct. $\tau_1$ .	Diffused. $\tau_2$ .	Total. $\tau$ .
Blotting-paper .....	2·7 per cent.	6·5 per cent.	9·2 per cent.
Cartridge-paper .....	2·5    "	8·7    "	11·2    "
Tracing-cloth .....	13·4   "	41·0   "	54·4   "
Tracing-paper .....	29·8   "	46·2   "	76·0   "

We may now collect the coefficients  $\eta$ ,  $\alpha$ ,  $\tau$ , determined by the foregoing independent methods, and compare their sum with unity.

TABLE VIII.

	$\eta$ .	$\alpha$ .	$\tau$ .	$\eta + \alpha + \tau$ .
Blotting-paper .....	82 per cent.	13·8 per cent.	9·2 per cent.	105·0 per cent.
Cartridge-paper ...	80    "	12·2    "	11·2    "	103·4    "
Tracing-cloth .....	35    "	15·0    "	54·4    "	104·4    "
Tracing-paper .....	22    "	7·0    "	76·0    "	105·0    "

The numbers in the last column differ from the true value of 100 per cent. to a greater extent than can fairly be accounted for by the limits of experimental error. They are all over 100; and this was the case, not only for the tests here given, but also for every one of many sets of tests taken. The small discrepancy would be accounted for by assuming that the law of cosines is not exactly fulfilled. A very slight departure from this law would be amply sufficient to explain the results.

Suppose the candle-power of a unit area of a diffusing surface in the direction of the normal is  $B$ , and in any direction  $\phi$  is

$$B(\cos \phi)^{1+\epsilon}.$$

It is then easy to show that the total amount of light given out per unit area is equal to

$$\pi B \frac{1}{1 + \frac{\epsilon}{2}}.$$



In all the above experiments the actual measurements have referred to the light receding from the diffusing substance at inclinations all practically normal to its surface. The quantity  $B$  has been measured, the total light has been calculated as  $\pi B$ , and has been overestimated in the ratio  $1 + \frac{\epsilon}{2} : 1$ .

To account for an error of 5 per cent., the quantity  $\epsilon$  need only be 0.1. The brightness of the surface (in the physiological sense) would, when viewed at an inclination  $\phi$ , be proportional to

$$B (\cos \phi)^{1+\epsilon}/\cos \phi, \quad \text{or} \quad B (\cos \phi)^\epsilon.$$

This quantity is practically constant (if  $\epsilon=0.1$ ) until  $\phi$  becomes very large. Its value is .994 for  $\phi=20^\circ$  and .974 for  $\phi=40^\circ$ , and the change in the brightness of the surface would hardly be perceptible to the eye.

This correction applies to the coefficients  $\eta_2$  and  $\tau_2$ ; it does not affect the values of  $\eta_1$ ,  $\alpha$ , or  $\tau_1$ . In some of the first tests of reflecting-power the inclination of the light-rays to the surface was considerably less than 90 degrees, and the values of  $\eta$  obtained were less than those given above. These tests confirm the idea that the cosine law is not strictly fulfilled, but they were not accurate enough to be conclusive.

The above measurements were all made in the Optical Laboratory of the Central Institution, and the writer has had the benefit of the assistance of some of the students of that College in re-testing and confirming the results given in the foregoing tables.

#### DISCUSSION.

Mr. A. P. Trotter said he had been interested in the subject of diffusion for many years with a view to obviating the glare of arc lamps. The reflecting-power of substances was of great importance in the illumination of rooms; in one case, measured by Dr. Sumpner and himself, two-thirds of the total illumination was due to the walls. Referring to the cosine law, he said he had found it true except when the angles of incidence approached  $90^\circ$ . In cases where considerable total reflexion took place, the apparent brightness near the normal direction was greatly in excess of that

in other directions. These points he illustrated by polar curves. He had also considered what should be the nature of a roughened or grooved surface to give the cosine law of diffusion. No simple geometrical form of corrugations, &c., seemed to fulfil the required conditions.

Dr. Hoffer said the high numbers given for the reflecting-powers of substances were very interesting. Most people had noticed the effect of laying a white table-cloth in an ordinary room. He had also observed that wall-papers of the same pattern, but slightly different in colour, had very different effects in producing increased illumination, and wished to know if the influence of small differences in colour and texture on diffusing-power had been investigated.

Mr. Blakesley defended the cosine law, and suggested that the summation of the powers exceeding unity might be due to the fact that the enclosure reflected heat as well as light, thus raising the temperature and increasing the efficiency of the radiant.

Dr. C. V. Burton did not understand why the cosine law should be objected to, for it was possible that no surface was perfectly diffusive. The effect of reflexion from walls, &c., say in illuminating a book, would not, he thought, be so great as would appear from the numbers given, for one usually read near a light and the reflected light falling on the book was only a small part of the whole, on account of the greater distances of the walls.

Dr. Sumpner in reply said he had, as stated in the paper, used white blotting-paper as a standard of reflecting-power and found it very convenient. His most careful measurements had been made on whitish surfaces and not on coloured ones. Where one colour, say red, preponderates in a room, the average light would be much redder than that emitted by the source, owing to the other colours being absorbed. In considering illumination as related to distinct vision, it was necessary to take account of the eye itself, for the pupil contracted in strong lights and opened in feeble ones. This subject he hoped to treat fully in a subsequent paper.

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IV. *The Laws of Molecular Force.*

By WILLIAM SUTHERLAND, M.A., B.Sc.\*

198  
 IN my last paper on this subject (Phil. Mag. April 1889) it was shown that if the law of force between two similar molecules is  $3Am^2/r^4$ , the parameter A could be calculated for a large number of bodies from Robert Schiff's measurements of their surface-tensions, and a law was announced connecting the values of A with chemical composition; but as this law was affected with exceptions in the case of the organic bromides and iodides and the amines, and as the argument from surface-tension requires the introduction of a considerable number of assumptions, I felt that it was very desirable to secure some other means of finding A. It soon appeared that the only satisfactory plan would be to return again to the search for the true characteristic equation of fluids on the model of Clausius's virial equation, as I had found that not one of those hitherto advanced was capable of general application. Fortunately the experimental material now available is so abundant and so well placed that I was completely successful in the quest, in the more tedious parts of which I had the advantage of assistance from my brother, Mr. John Sutherland. Amagat's exhaustive study of the compression and expansion of gases, along with Ramsay and Young's work on ethyl oxide, were the groundwork of the research.

As the true characteristic equations for fluids are the key to many chambers of molecular physics, I have been able to enter many of these, and especially to discover the true law of the parameter A without exception. To give an idea of the scope of these investigations free from detail, I furnish the following table of contents:—

1. Establishment of characteristic equation for compounds above the region of the critical volume, with proof that there is discontinuity in the liquefaction of compounds.
2. The same for the gaseous elements, with proof of continuity during liquefaction in their case.
3. Brief discussion of exceptional compounds such as the alcohols and ethylene.
4. Establishment of characteristic equation below the region of the critical volume, its main feature being the occurrence

\* Read June 24, 1892.



in it of the same internal virial constant as in the equation for the region above the critical volume.

5. A short digression on the general interpretation of Clausius's equation of the virial.

6. Consideration of Van der Waals's generalization that if each substance has its temperature, pressure, and volume expressed in terms of the critical values as units, one and the same law applies to all bodies; proof that this is true for elements and compounds separately, above the critical region, and approximately true below.

7. Five methods of finding the internal virial constant: first, from the expansion and compression of the substance as gas or vapour; second, from its expansion and compression as liquid; third, from its latent heat; fourth, from its critical temperature and pressure; fifth, from its surface-tension: all the methods being afterwards proved to give accordant results for a large number of compounds.

8. The fifth or capillary method treated in greater detail, with digressions on the Brownian movement and molecular distances.

9. Establishment on theoretical grounds of Eötvös's relation between surface-tension and molecular domain (volume).

10. Tabulation for a large number of bodies of the product of the square of the molecular mass by the virial constant determined by several methods, and verification thereby of the general principles preceding.

11. Establishment of the law connecting the virial constant of a substance with its chemical composition. Definition of the Dynic Equivalent of a substance and determination of its value for several radicals.

12. Close parallelism between Dynic Equivalents and Molecular Refractions.

13. Return to the discontinuity during liquefaction of compounds, and proof that it is due to the pairing of molecules.

14. Brief discussion of the constitution of the alcohols as liquids.

15. Methods of finding the virial constant for inorganic compounds, including a theory of the capillarity and compressibility of solutions.

16. Tabulation of the product of the square of the molecular mass by the virial constant for inorganic compounds, and determination of the Dynic Equivalents of the metals in the

combined state. Again a close parallelism between dynic equivalents and molecular refractions or refraction-equivalents.

17. Meaning of this parallelism ; general speculations as to the volumes of the atoms and their relation to ionic speeds.

18. Attempt to determine the velocity of light through the substance of the water-molecule.

19. Suggested relation between the change in the volume of an atom on combination and the change in its chemical energy.

1. *Establishment of the characteristic Equation for Compounds above the region of the Critical Volume*, with proof that there is discontinuity in the liquefaction of compounds.—Amagat established (*Ann. de Chim. et de Phys.* sér. 5, t. xxii.) that for gases  $\partial p/\partial T$  is a function of volume only down to volumes near the critical, but that at lower volumes it begins to vary with temperature. Ramsay and Young (*Phil. Mag.* May 1887), while verifying the independence of  $\partial p/\partial T$  on temperature above the critical volume for such bodies as ethyl oxide and the alcohols, sought to show that this independence continues right into the liquid state ; but, as a matter of fact, their temperature-range in the experiments below the critical volume is not great enough to decide the question one way or another. We shall see that in the case of compounds Amagat's conclusion is the correct one, while in the case of the elements Ramsay and Young's contention appears to hold. The conviction that  $\partial p/\partial T$  becomes slightly variable with temperature below the critical volume was one reason that determined me to represent the behaviour of fluids by two equations merging into one another ; the one applying down to near the critical volume, the other below that.

Clausius's equation of the virial is to be our guide in studying  $\partial p/\partial T$ ,

$$\frac{3}{2}pv = \Sigma \frac{1}{2}mV^2 - \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma Rr,$$

where  $V$  is velocity and  $R$  is force between two molecules at distance  $r$  apart.

According to the law of the inverse fourth power, the double sum of the internal virial reduces to an expression varying inversely as the volume and independent of the temperature, as I have shown before (*Phil. Mag.* July 1887).

If we integrate Amagat's relation  $\partial p/\partial T = f(v)$ , we get

$$p = f(v)T + \phi(v);$$

and as in the perfect gaseous state  $pv = RT$ , where  $v$  being the volume of unit mass and  $T$  reckoned as temperature  $C. + 273^{\circ}$ ,  $R$  varies inversely as the molecular weight of the substance, we will write our equation in the form

$$pv = RTvf(v) + v\phi(v),$$

where we see that  $v\phi(v)$  stands for the internal virial-term. If, then, according to the law of the inverse fourth power, the internal virial varies inversely as  $v$ , then  $v^2\phi(v)$  ought to be constant. Now Ramsay and Young have carefully tabulated the values of  $Rvf(v)$  and  $\phi(v)$  for different values of  $v$  in the case of ethyl oxide; so it is easy to tabulate  $Rvf(v)$  and  $v^2\phi(v)$ , as we proceed to do in the following Table, where  $v$  is the volume of a gramme of ethyl oxide in cubic centimetres, and the metre of mercury is the unit of pressure. These units will be used throughout when we are dealing with experimental results involving pressures; but when necessary, for theoretical convenience, we will convert to absolute units.

TABLE I.—Ethyl Oxide.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	·842		3·3	1·758	2413
100	·912	5710	3·0	1·865	2366
50	·973	5190	2·75	2·013	2371
20	1·129	4554	2·5	2·30	2487
15	1·201	4302	2·4	2·42	2519
10	1·327	3908	2·3	2·56	2550
8	1·409	3661	2·2	2·73	2589
6	1·525	3308	2·1	2·95	2646
5	1·595	3047	2·0	3·19	2691
4	1·654	2656	1·9	3·54	2771
3·7	1·682	2534			

The critical volume of ethyl oxide is between 5 and 4; so that if  $\partial p/\partial T$  does become variable with temperature below the critical volume, the values of  $Rvf(v)$  and  $v^2\phi(v)$ , calculated for volumes below 5, on Ramsay and Young's assumption that even below the critical volume  $\partial p/\partial T$  is independent of temperature, will be affected with an error of more or less importance; they may therefore be regarded as a first approximation only and are added for comparison.

The first point to notice in these numbers is that  $Rvf(v)$  increases steadily from its limiting value ·842 in the perfect gas state to double that amount near the critical volume, while

at the same time  $v^2\phi(v)$  diminishes from its limiting value in the gaseous state to the half of it near the critical volume. This result would seem at once to contradict the law of the inverse fourth power; but we shall see in the sequel that, in compression down to the critical region, there is a process of pairing going on among the molecules and producing this departure from the requirements of the law of the inverse fourth power, uncomplicated by such a process.

It is to be noted that the limiting value of  $v^2\phi(v)$  is difficult to determine experimentally, because  $\phi(v)$ , the quantity measured, tends to the limit zero. But while below volume 4,  $Rvf(v)$  increases with increasing rapidity,  $v^2\phi(v)$  remains almost stationary, it dips a little and then increases; but remembering that its values count only as first approximations, we may assume that  $v^2\phi(v)$  attains near the critical volume a value which remains constant in the liquid state, and is about half of the limiting value for the gaseous state. Thus there is discontinuity in the passage from the region above the critical volume to that below (or, more briefly but less accurately, during liquefaction). We must note carefully that in the range of volume from 4 to 1.9, which is a large liquid range,  $v^2\phi(v)$  remains constant, as it should according to the law of the inverse fourth power, now that the process of pairing is completed.

To represent  $Rvf(v)$  I found the form  $R\{1 + 2k/(v+k)\}$  to be efficient; it gives the limit  $2R$  to the function when  $v=k$ ; and as .842 is the known value of  $R$ , each of the above tabulated values of  $Rvf(v)$  yields a value of  $k$ , the mean value 4.066 having been adopted by me. The other function,  $v^2\phi(v)$ , proved no less amenable to simple representation, the form found to fit it being  $lv/(v+k)$ , which attains the value  $l/2$  when  $v=k$ ; and as the value of  $k$  is known, we can calculate from each tabulated value of  $v^2\phi(v)$  a value of  $l$ , and again adopt the mean value 5514. Hence down to near the critical volume we have the behaviour of ethyl oxide represented by the simple form of equation

$$pv = RT \left( 1 + \frac{2k}{v+k} \right) - \frac{l}{v+k}, \text{ with } k=4.066 \text{ and } l=5514,$$

involving only the two constants  $k$  and  $l$  peculiar to ethyl oxide.



We will now compare a few values of the pressures, in metres of mercury, given by this equation with those found by Ramsay and Young.

TABLE II.

	Volume .....	100.	50.	20.	10.	6.
175° C. {	Pressure, experiment.	3·500	6·620	13·88		
	Pressure, calculated.	3·538	6·634	13·78		
195° C. {	Pressure, experiment.	3·710	7·020	15·06	23·00	27·00
	Pressure, calculated.	3·719	7·021	14·90	22·99	27·44
280° C. {	Pressure, experiment.	.....	.....	19·80	34·59	49·62
	Pressure, calculated.	.....	.....	19·69	34·28	49·00

The agreement is as close as can be looked for; because although Ramsay and Young measure volumes to within ·01 centim., and pressures to within 2 centim. of mercury, the quantities measured cannot be considered known with that degree of accuracy; for the discrepancies between their measurements and those of Perot (*Ann. de Chim. et de Phys.* ser. 6, t. xiii.), who made special determinations in a large globe of the saturation-volume of ethyl oxide at different temperatures, are greater than those in Table II. Accordingly it would be useless to seek a better empirical representation of Ramsay and Young's results than the above; and as we are chiefly interested in establishing our simple form of characteristic equation, we had better proceed at once to the consideration of Amagat's experiments on carbonic dioxide, practically identical with Andrews's, but more extensive. Amagat's unit of volume is  $\frac{1}{3410}$  of that occupied by the gas at 0° and 1 atmosphere; taking the weight of a litre of the gas at 0° and 1 atmosphere as 1·9777 gramme, we can convert Amagat's data to the gramme and centim. as units. The following Table is arranged in the same way as Table I. :—

TABLE III.—Carbonic Dioxide.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	1.421		2.64	2.56	1661
7.34	1.92	2159	2.35	2.64	1566
(7.00)	(2.11)	(2500)	2.05	2.77	1482
5.14	2.13	2071	1.91	2.86	1441
(5.00)	(2.37)	(2400)	1.76	3.02	1430
3.67	2.31	1858			

(The bracketed numbers are introduced from Andrews.)

A glance at this Table shows the same facts to be in it as in Table I. The critical volume of  $\text{CO}_2$  is somewhere about 2; and we notice that near this volume  $Rvf(v)$  tends to double the value 1.421 in the gaseous state, while at the same point  $v^2\phi(v)$  approaches a constant value about the half of what must from inspection be estimated as the upper limit of it. Both functions are accurately represented by the same forms as in the case of ethyl oxide with  $k=1.762$  and  $l=2773$ . With these values the following pressures were calculated for comparison with experiment:—

TABLE IV.—Carbonic Dioxide.

	Volume .....	11.74.	8.8.	5.87.	3.67.	2.64.	2.20.
100° C. {	Pressure, experiment.	39	49.8	69	96.8	124	143
	Pressure, calculated.	39.4	50.4	70	99	123	137
70° C. {	Pressure, experiment.	34.5	43.7	58.8	79.5	95	105
	Pressure, calculated.	34.8	44.0	59.4	80.0	94	100
35° C. {	Pressure, experiment.	29.7	36.5	46.4	55.8	61	63.6
	Pressure, calculated.	29.5	36.5	47.0	57.5	60	57.7

The agreement is quite satisfactory except at the lowest volume, which is near the critical; and I have shown (Phil. Mag. August 1887) that near the critical point in capillary tubes the relation of pressure to volume becomes fickle, the

measurements of Andrews and Amagat differing from one another as much as experiment and calculation in Table IV. To illustrate this at higher volumes I introduced into Table III. a couple of Andrews's values of  $Rvf(v)$  and  $v^2\phi(v)$ , from values of  $Rf(v)$  and  $\phi(v)$  calculated by Ramsay and Young (Phil. Mag. 1887), after conversion of Andrews's air-manometer indications to true metres of mercury. It will be seen that Andrews makes  $\partial p/\partial T$  a little larger than Amagat; and this being so, it is not worth while to seek for closer agreement than that in Table IV., at least at present.

We have, however, a sensitive means of determining whether the form and the values of the constants adopted truly represent the behaviour of  $\text{CO}_2$  closely enough at high volumes,—namely, Thomson and Joule's and Regnault's experiments on the cooling of  $\text{CO}_2$  when it escapes through a porous plug from under pressure (Phil. Trans. 1854–1862; *Mém. de l'Acad.* xxxvii.). Natanson (Wied. Ann. xxxi.) has repeated the Joule and Thomson experiments on  $\text{CO}_2$  under the more favourable conditions afforded by the commercial sale of the fluid in large quantity and great purity, so that he has been able to measure not only the cooling effect for a given pressure excess, but also its variation with pressure. Taking all these experiments together, we have a delicate test for the equation at high volumes.

The most convenient expression for the cooling effect for our present purpose is

$$K_p \frac{d\delta}{dp} = \theta \frac{dv}{d\theta} - v;$$

where  $\delta$  is the cooling effect,  $K_p$  is the specific heat at constant pressure, and  $\theta$  is temperature on the absolute thermodynamic scale. In previous papers I took from Joule and Thomson's original investigation  $\theta = T + .7^\circ$ , not then aware that Sir W. Thomson, in his article "Heat" (*Encyc. Brit.*), had by a fuller discussion of all the experimental data proved  $\theta = T$ , and so removed the difficulty that the term  $.7$  opposed to the harmony of the thermodynamic and molecular kinetic conceptions of temperature.

With our characteristic equation the cooling effect is, after the appropriate reductions, given by

$$K_p \frac{d\delta}{dp} = 2(l/RT - k) + p \left\{ 4(l/RT - k)(l/RT - 2k) - 2k(l/RT - 2k) - lk/RT \right\} / RT.$$

Within Joule and Thomson's range of pressure this can be reduced to

$$K_p \frac{d\delta}{dp} = 2(l/RT - k) ;$$

and  $d\delta$  can be made to stand for the integral cooling effect if  $dp$  stands for the integral excess of 2·54 metres of mercury, to which they reduced their results. The term in  $p$  will be taken account of when we come to Natanson's results. From Regnault's data we have, in dynamical measure

$$K_p = 424(\cdot 187 + \cdot 00027 t).$$

TABLE V.

(Cooling effect of  $\text{CO}_2$  escaping through a porous plug under a pressure excess of 2·54 metres of mercury.)

Temperature C....	7°·4.	8°.	19°·1.	35°·6.	54°.	91°·5.	93°·5.	97°·5.
Th. and Joule ...	4·4	4·2	3·9	3·4	2·95	2·35	2·16	2·13
Calculated .....	4·4	4·4	4·1	3·7	3·4	2·7	2·7	2·6
Temperature C.	-25°	3°.	100°.					
Regnault .....	6·3	4·1	2·6					
Calculated .....	5·5	4·5	2·6					

The agreement is as good as possible if both sets of experiments are taken into consideration. But Natanson's result affords a more delicate test; he found that at 20° up to 25 atmospheres the cooling effect for a pressure excess of one atmosphere could be represented by

$$\frac{d\delta}{dp} = 1\cdot 18 + \cdot 0126 p ;$$

while the theoretical equation above gives

$$\frac{d\delta}{dp} = 1\cdot 23 + \cdot 012 p,$$



which is practically identical with Natanson's. On account of the closeness of this agreement we obtain as an indirect conclusion, that the experimental work on  $\text{CO}_2$  taken as a whole makes the absolute thermodynamic zero  $-273^\circ$ , the same result as Sir W. Thomson has obtained for air and H in the article "Heat" (*Encyc. Brit.*), while for  $\text{CO}_2$ , using only Regnault's coefficient of expansion and Joule and his own cooling effects, he found  $-273^\circ\cdot9$ . Now that  $\text{CO}_2$  is seen to be in harmony with the other two more perfect gases, the number 273 may be accepted definitely as the absolute temperature of melting ice.

The equation therefore applies accurately at high volumes, a fact which we can prove by another test, seeing that Amagat carried out a special research (*Compt. Rend.* xciii.) to determine the ratios of  $pv$  to  $p'v'$  at different temperatures and up to values of  $p'$  about 8 atmospheres,  $v$  being double  $v'$ .

TABLE VI.

(Values of  $pv/p'v'$  at high volumes for  $\text{CO}_2$ .)

( $p=5\cdot7$  metres of mercury :  $v=2v'$ .)

Temperature C. ....	50°.	100°.	200°.	300°.
Amagat .....	1·0145	1·0087	1·0040	1·0020
Calculated.....	1·0156	1·0092	1·0026	1·0000

As the experiments are not free from liability to an error of 1 in 1000, the agreement is again close enough to prove the applicability of the equation at high volumes.

In the sequel it will be shown that this equation applies to the great majority of compounds, but meanwhile the only other experimental determinations similar to those already discussed for ethyl oxide and carbonic dioxide are Amagat's for  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CH}_4$ , and  $\text{C}_2\text{H}_4$ ; Roth's for  $\text{SO}_2$  and  $\text{NH}_3$  (*Wied. Ann.* xi.); Janssen's for  $\text{N}_2\text{O}$  (*Wied. Beibl.* ii.); and Ramsay and Young's on methyl and ethyl alcohol (*Phil. Mag.* Aug. 1887). Our form of characteristic equation applies to  $\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$  successfully, but not to  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and

$\text{CH}_4$ , which require a still simpler type, the alcohols on the other hand requiring a less simple type. These are the values of  $k$  and  $l$  for  $\text{SO}_2$ ,  $\text{NH}_3$ , and  $\text{N}_2\text{O}$  :—

	$\text{SO}_2$ .	$\text{NH}_3$ .	$\text{N}_2\text{O}$ .
$k$ . .	2.08	4.8	2.3
$l$ . .	2740	22040	3420

with which the following pressures have been calculated for comparison with the experimental data, the latter being taken direct from air or nitrogen manometer without correction for departure from Boyle's law.

TABLE VII.

$\text{SO}_2$ at $99^\circ 6$ .			$\text{NH}_3$ at $99^\circ 6$ .			$\text{N}_2\text{O}$ at $25^\circ 1$ .		
$v$ .	$p$ exp.	$p$ calc.	$v$ .	$p$ exp.	$p$ calc.	$v$ .	$p$ exp.	$p$ calc.
41.9	7.9	8.0	172	7.6	7.6	7.0	39.1	37.2
17.6	17.1	17.0	85.7	14.8	14.7	5.36	42.6	42.4
13.6	21.2	20.8	65.4	18.8	18.9	3.78	43.9	46.7
9.9	26.0	26.2	40.0	28.6	29.1			
At $183^\circ$ .			At $183^\circ$ .			At $43^\circ 8$ .		
18.2	21.7	22.0	160	10.3	10.2	5.86	49.4	47.9
10.0	37.3	36.9	81.6	19.8	19.6	4.62	55.6	54.4
4.58	69.2	67.5	36.1	40.9	42.1	3.47	61.4	61.0
2.75	98.2	93.5	16.2	82.6	85.4	2.82	64.1	64.3

This comparison has been made only to show that the form is applicable to other bodies as well as to ethyl oxide and carbonic dioxide ; full confirmation of the form will come later on, in the study of many of its applications.

2. *Establishment of the Characteristic Equation for the Gaseous Elements*, with proof of continuity during liquefaction. —The simplest plan in the case of the gaseous elements will be to take nitrogen as typical and tabulate for it  $Rvf(v)$  and  $v^2\phi(v)$  from Amagat's experiments up to 320 metres of mercury.

TABLE VIII.—Nitrogen.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas	2.233		4.15	3.25	1188
9.22	2.63		3.69	3.40	1007
6.91	2.77	1197	3.46	3.44	982
5.76	3.08	1396	3.23	3.80	1250
4.61	2.94	809			

The values of  $v^2\phi(v)$  are unsteady, because the departures from Boyle's law are so small that  $\phi(v)$  cannot be determined with accuracy; but it is clear enough that  $v^2\phi(v)$  does not tend to diminish within the range of volume available, not a wide enough one, however, to convince us that there is a radical difference between the course of this function in elements and compounds. But if we adopt from this Table as it stands the only possible conclusion that  $v^2\phi(v)$  is constant, we shall be able to justify it by its consequences. In contrast to the constancy of  $v^2\phi(v)$  is the tendency of  $Rvf(v)$  at low volumes to double its perfect gas-value.

In the case of  $H_2$  and  $O_2$  the two functions run a similar course to that for  $N_2$ , but it is a more unexpected fact that they also do the same for the compound methane,  $CH_4$ , as is shown in Table IX.

TABLE IX.—Methane.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	3.908		12.11	5.24	6900
32.3	4.16		10.09	5.43	6400
28.2	4.30	5600	8.07	5.95	6500
24.2	4.39	6200	7.27	6.47	7000
20.2	4.73	6900	6.46	6.80	6800
16.1	4.73	6200	6.05	6.73	6200

It is evident that we have here to do with  $v^2\phi(v)$  as a constant, that is with an internal virial varying inversely as the volume down to near the critical volume, and  $Rvf(v)$  tending somewhere near that point to about double its value in the perfect

gas state. The course of  $Rvf(v)$  in these four gases is represented by the simple form

$$R \left\{ 1 + \frac{k}{2} / \left( v - \frac{k}{2} \right) \right\},$$

which attains the value  $2R$  when  $v=k$ . Hence the characteristic equation down to  $v=k$  is

$$pv = RT \left( 1 + \frac{\frac{k}{2}}{v - \frac{k}{2}} \right) - \frac{l}{v},$$

a form which I had already adopted for air (Phil. Mag. Aug. 1887). The following are the values for  $k$  and  $l$  :—

	H.	N <sub>2</sub> .	O <sub>2</sub> .	CH <sub>4</sub> .	Air.
$k$ . .	12.0	2.64	1.78	5.51	2.47[2.11]
$l$ . .	41700	1175	851	6460	1110[910]

The values given in brackets for air are those previously found by me from Amagat's data (*Compt. Rend.* xcix.), but as these data are not carried to such high pressures as those for N<sub>2</sub> and O<sub>2</sub>, I have calculated values for air by adding to four fifths of the values for N<sub>2</sub> one fifth of the values for O<sub>2</sub>.

This equation is almost identical with that of Van der Waals, but it is a little simpler. It gives the following pressures for comparison with Amagat's experimental results :—

TABLE X.

Hydrogen. At 17.7° C.			Nitrogen. At 17.7° C.			Oxygen. At 14.7° C.		
$v$ .	$p$ exp.	$p$ calc.	$v$ .	$p$ exp.	$p$ calc.	$v$ .	$p$ exp.	$p$ calc.
166.9	57.5	56.9	13.83	46	45.7	5.73	88.9	89.7
100.1	99	99	6.91	92	91	3.58	141	142
60.1	176	176	4.61	145	142	2.58	201	203
46.7	238	241	3.69	194	188	2.43	216	219
			3.23	223	226			
At 100° C.			At 100° C.			At 100° C.		
166.9	74.2	73.3	13.83	60	60.5	5.73	123	124
100.1	129	128	6.91	125	124	3.58	204	204
60.1	230	229	4.61	200	199	2.58	300	301
46.7	311	315	3.69	270	266	2.43	322	327
			3.23	320	323			



The experimental numbers for oxygen are taken from Amagat's data in the *Comptes Rendus*, xci.

The most delicate test we can apply to our form at high volumes is, in the case of air, to compare the calculated with the experimental Thomson and Joule cooling effect. When I did this with the previous equation for air ( $k=2.11$  and  $l=910$ ), I assumed the difference  $.7^\circ$  to exist between the melting-point of ice on the thermodynamic and gas thermometers; but, as already pointed out, Sir W. Thomson having proved this difference not to exist, there must have been a compensation of errors in the application of the previous equation. Thomson's expression for the cooling effect, applied to our equation for air, becomes

$$K_p d\delta/dp = 2l/RT - k/2,$$

which gives the following calculated values :—

Cooling effects of air escaping through a porous plug into the atmosphere under a pressure excess of 2.54 metres of mercury.

Temperature C.....	7°1.	17°.	39°5.	92°8.
Experiment . . .	.88	.86	.75	.51
Calculation . . .	.84	.80	.71	.55

The agreement is the closest to be looked for, and proves the accuracy of our equation for air at high volumes.

At low volumes we can test the form for all the elementary gases and  $\text{CH}_4$  by applying it to the calculation of the critical volume, pressure, and temperature in each case. To do this at the present stage we must assume that our form can be trusted to hold not only to the critical volume but also a little past into the liquid region, a legitimate assumption for the elements, where we have seen the internal virial varying inversely as the volume, and so giving a guarantee of continuity, but not legitimate for the compounds where discontinuity occurs. Then, applying James Thomson's idea of the passage from the gaseous to the liquid state, as precisionized by Maxwell and Clausius, we have the critical point determined by the conditions  $\partial p/\partial v=0$ ,  $\partial^2 p/\partial v^2=0$ .

Along with the characteristic equation these lead to the fol-

lowing values:—critical volume  $v_c = 3k/2$ ; critical temperature  $T_c = 16l/27Rk$ ; critical pressure  $p_c = 4l/27k^2$ ,—to compare with the experimental values found by Olszewski for  $O_2$  and  $N_2$  (*Compt. Rend. c.*), by Wroblewski for air, and by Dewar for  $CH_4$  (*Phil. Mag.* 1884, xviii.).

TABLE XI.

		$H_2$ .	$N_2$ .	$O_2$ .	$CH_4$ .	Air.
Critical Volume.	{ exper. ...	.....	3.4	2.5		
	{ calc. ....	.....	3.96	2.67		
Critical Temperature.	{ exper. ...	.....	-146	-119	-99.5	-140
	{ calc. ....	-229	-155	-127	-95	-149
Critical Pressure.	{ exper. ...	.....	27	38	37	30
	{ calc. ....	19	25	40	32	27

The agreement is all that can be looked for in view of the difficulties of measuring these low critical temperatures and their associated pressures. With regard to hydrogen all we know is that Olszewski (*Compt. Rend. ci.*) has submitted it to a temperature estimated by him as  $-220^\circ$  without a sign of liquefaction. If our equation is to be trusted, it would indicate that he would need to go some 10 degrees lower before the only unliquefied gas is conquered. Wroblewski has published data on the compressibility of  $H_2$  up to pressures of 70 atmospheres at temperatures of  $-103^\circ$  and  $-182^\circ$  (*Journ. Chem. Soc.* 1889), and with these our equation is in accord, but there is hardly need of tabulated proof.

3. *Brief discussion of exceptional Compounds such as the Alcohols and Ethylene.*—To complete our survey of the experimental material on bodies above the critical region we have to consider Ramsay and Young's observations on methyl and ethyl alcohol, and Amagat's on ethylene. Ramsay and Young point out that at low volumes the values of  $\partial p/\partial T$  for the alcohols are not so reliable as for ethyl oxide, being determined from a smaller temperature range; hence our values of  $Rvf(v)$  and  $v^2\phi(v)$  are not so reliable as before, but they suffice to show the exceptional nature of these bodies.

TABLE XII.—Methyl Alcohol.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	1.950		25	3.50	24800
340	2.14		20	3.70	23000
240	2.32	45500	18	3.79	22000
200	2.40	48000	16	3.97	21700
170	2.46	46100	14	4.18	20900
135	2.56	43700	12	4.38	19900
100	2.70	41000	11	4.46	19000
70	3.04	42100	10	4.53	17900
50	3.10	33500	9	4.58	16700
40	3.20	30200	8	4.55	15000
30	3.37	26800	7	4.39	12900

## Ethyl Alcohol.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	1.35		8	3.43	11300
108.2	1.65	18000	6	3.34	8600
53.4	1.83	15000	4	3.37	6200
30	2.16	15000	3	3.51	5000
26.1	2.31	16000	2.4	3.93	4600
18.2	2.83	17000	2	4.87	4700
12	3.32	15000	1.8	5.83	4900
10	3.41	13500	1.6	7.06	4900
9	3.43	12500	1.4	8.81	4700

The numbers for methyl alcohol do not extend as far as the critical volume, while those for ethyl alcohol go considerably beyond it, lying as it does between 3 and 4; but we notice in both cases that  $Rvf(v)$  increases from the limiting gaseous value, but attains a practically constant value before the critical volume is reached. In ethyl alcohol we may say that the value 3.4 is retained from volume 10 to volume 3, and moreover this 3.4 is not now double the initial 1.35, but about 2.5 times it. In methyl alcohol the value 4.5 may be said to be retained constant from volume 11 to 7, the lowest on the table; so that it is probable that, as in the case of ethyl alcohol, this value will be retained down to the critical volume: here again, also, the 4.5 is more than double the initial 1.95, but is only 2.3, not 2.5, times it.

Note that, in ethyl alcohol, as soon as the critical volume is

passed  $Rvf(v)$  begins again to increase rapidly, just as happened in the case of ethyl oxide. But for our present purpose more interest attaches to the course of  $v^2\phi(v)$ . In methyl alcohol at high volumes it seems to approach a limit which we may assign as 46,000, and then at volume 16, where  $Rvf(v)$  has risen to double its initial value,  $v^2\phi(v)$  has fallen to almost half of 46,000, but as  $Rvf(v)$  continues to rise  $v^2\phi(v)$  continues to fall, and still continues to do so even when  $Rvf(v)$  has become constant. In methyl alcohol we cannot follow the changes right down to the critical volume, but in ethyl alcohol we see that  $v^2\phi(v)$  attains at the critical volume a value which is carried constant into the liquid state, this constant value being about one quarter of the apparent limiting value 20,000 at large volumes. The constancy of  $v^2\phi(v)$  below the critical volume is in striking contrast to the rapid variation of  $Rvf(v)$ .

I have not sought to represent by formulas the course of the two functions for the alcohols, as I have doubts about  $\partial p/\partial T$  being independent of temperature in the case of the alcohols; if it is variable then the values of our functions are affected with error. In any case we have seen that above the critical region the alcohols behave differently from our two typical compounds, ethyl oxide and carbonic dioxide; in section 14 it will be seen that in the liquid region, on the other hand, the alcohols approach the regular compounds in many respects, but are still exceptional in others. There remains now only ethylene to consider as to its gaseous behaviour.

TABLE XIII.—Ethylene.

$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .	$v$ .	$Rvf(v)$ .	$v^2\phi(v)$ .
Perfect gas.	2.22		4.61	4.15	4500
20.75	2.71	5800	4.15	4.45	4500
16.14	2.78	5320	3.69	4.81	4400
11.53	3.07	5500	3.22	5.71	4700
9.23	3.24	5300	2.77	6.41	4400
6.92	3.58	5100	2.65	6.63	4200
5.76	3.83	4900	2.54	7.87	5000

According to Cailletet and Mathias (*Compt. Rend.* cii.), the critical volume of ethylene is about 4.5; so that, again, in



the above table we see  $Rvf(v)$  near the critical volume attaining double its initial value and increasing rapidly thereafter. Once more, too, we see  $v^2\phi(v)$  attaining near the critical volume a value which it retains constant below; but ethylene is exceptional in that this value is not half the limit at high volumes. The facts in the above table may be summarized in the statements that  $Rvf(v)$  may be represented by the form  $R(1+k/v)$ , and  $v^2\phi(v)$  by the form  $vl/(v+a)$ ; so that the characteristic equation for ethylene is

$$pv = RT \left( 1 + \frac{k}{v} \right) - \frac{l}{v+a},$$

with  $k=4.15$ ,  $a=1.64$ , and  $l=6270$ .

The form for ethylene is intermediate in simplicity between that for the simple gases and that for compounds, except that it has an extra constant. It is also worth noting that the forms

$$\frac{k}{2} \left/ \left( v - \frac{k}{2} \right) \right., \quad k/v, \quad \text{and} \quad 2k/(v+k)$$

are special cases of a general form

$$nk/\{v + (n-1)k\},$$

with  $n=\frac{1}{2}$ , 1, and 2.

4. *Establishment of Characteristic Equation below the region of the Critical Volume.*—Now that we have practically exhausted the available data of the gaseous state, we see that by themselves they do not give much scope for generalization; but if we can secure an equation applicable from the critical volume down to the volumes of liquids in the ordinary state, then, with two equations covering almost the whole range of fluidity, we shall have a much larger experimental area laid under contribution for information on the characters of molecules.

Already we have secured one important fact towards the acquisition of such an equation, namely that below the critical volume the internal virial term varies inversely as the volume; and in the case of ethyl oxide we know its actual amount  $l/2v$  with  $l=5514$ . We have therefore only to add to  $l/2v$  Ramsay and Young's values of  $pv$  at different temperatures for different

volumes below the critical, and we obtain the values of the kinetic-energy term in the desired equation; we can then proceed to study how this quantity depends on temperature and volume, and express the resulting conclusions in a formula.

As to the form we have this clue, that it must join on continuously with the previous one where that ceases to be applicable. Now the first fact to notice is that our form for compounds above the critical region cannot, like that for the elements, give a critical point by itself at all; for given  $p$  and  $T$  it is not a cubic but a quadratic in  $v$ , and hence cannot give us the three equal roots which are adopted as characteristic of the critical point when we apply the conditions

$$\partial p / \partial v = 0, \quad \partial^2 p / \partial v^2 = 0.$$

This emphasizes the discontinuity in compounds as contrasted with elements. However, we know as an experimental fact that at the critical point  $\partial p / \partial v = 0$ , which with the characteristic equation gives us only two relations between the critical temperature, pressure, and volume. As a third relation that would perfectly define these three quantities I was led to believe that the critical volume is proportional to  $k$ , and found that

$$\text{critical volume } v_c = 7k/6$$

is the relation which, with the two others, gives successfully the numerics of the critical state in agreement with experiment. As this will be proved subsequently (Section 10) for a large number of substances, I will not delay at present to give examples, except for those compounds for which we have already found  $k$  and  $l$ .

TABLE XIV.

Critical temperature,  $T_c = 120l/409Rk$ ; critical pressure,  
 $p = 36l/409k^2$ .

		(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O.	CO <sub>2</sub> .	SO <sub>2</sub> .	NH <sub>3</sub> .	N <sub>2</sub> O.
Critical Temperature.	{ exper. ...	194	32	155	130	35
	{ calc. ....	199	52	125	96	36
Critical Pressure.	{ exper. ...	27.1	59	60	87	57
	{ calc. ....	29.3	78.6	56	84	57

The want of accuracy in the agreement in parts of this table is to be ascribed partly to inaccuracy in the ordinary determinations of the critical point, as I have already pointed out that capillary action must sometimes largely affect the numerics of the critical state when these are determined in capillary tubes (Phil. Mag. August 1887). Regnault, in his account of his experiments on the saturation-pressures of  $\text{CO}_2$ , expressly declares that he had liquid  $\text{CO}_2$  at  $42^\circ$ , which is  $10^\circ$  above the apparent critical temperature in capillary tubes; and Cailletet and Colardeau (*Compt. Rend.* cviii.) have shown that although the meniscus between gas and liquid  $\text{CO}_2$  disappears to the eye about  $31^\circ$  or  $32^\circ$ , yet characteristic differences between liquid and gas can be proved to exist several degrees higher than this. Hence an error of at least  $10^\circ$  is possible in ordinary determinations of critical temperatures. On the other hand, an error of 5 per cent. in the value of an absolute temperature of about  $400^\circ$  as given by our equation would amount to  $20^\circ$ . Table XIV. is to be taken in the light of these facts.

We have now ascertained a second property that our equation for volumes below the critical is to possess: it must begin to apply when  $v=7k/6$ , as the other form cannot apply below this volume at the critical temperature. At this volume the kinetic-energy term in our form above the critical region becomes

$$RT(1+12/13), \text{ or } 25RT/13;$$

so that  $25R/13$  is the lower limit of the term which in the new equation is to take the same place as  $Rvf(v)$  hitherto. Hence for this term the form

$$25R(1+F(v))/13$$

naturally suggests itself, and as  $F(v)$  is to vanish when  $v=7k/6$ , we get  $(7k/6-v)/\psi(v)$  as a suggestion for its form; and it only remains from the data obtained, as I have said, by adding  $l/2v$  to Ramsay and Young's values of  $pv$  for volumes of ethyl oxide below  $k$ , to determine the form of the function  $\psi(v)$ . This was found, after a rather tedious search, to come out in the simple form

$$\sqrt{T}(v-\beta) B ;$$

so that finally we have the following as the equation for ethyl oxide below the volume  $k$  :

$$pv = R'T \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta} \right) - \frac{l}{2v},$$

with the following values for the constants :

$$R' = 25R/13, \quad k' = 7k/6, \quad B = 63 \cdot 1, \quad \beta = 1 \cdot 11,$$

$R, k, \text{ and } l \text{ as before.}$

I propose to call this the infracritical equation. It is to be noticed that we have introduced only two additional constants ; so that, as regards number of constants, we could hardly look for a simpler form.

Above the volume  $7k/6$  the appropriate form was proved to be

$$pv = RT \left( 1 + \frac{2k}{v + k} \right) - \frac{l}{v + k},$$

which I propose to call the supracritical equation.

Between  $k$  and  $7k/6$  we have the circacritical form

$$pv = R'T \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta} \right) - \frac{l}{v + k}.$$

This, then, gives the complete representation of ethyl oxide in the fluid state if we establish the sufficiency of the infracritical form, as we now proceed to do. In the next table are compared the pressures found by Ramsay and Young and those given by the equation.

TABLE XV.—Liquid Ethyl Oxide.

Volume .....	3·7.	2·75.	2·25.	2.	1·9.
195° C. { Pressure, exper. .	28	29	43		
"    calc. ...	32	26	45		
175° C. { Pressure, exper. .	.....	.....	19	43	
"    calc. ...	.....	.....	14	48	
150° C. { Pressure, exper. .	.....	.....	.....	.....	19·5
"    calc. ...	.....	.....	.....	.....	20

For the proper appreciation of this table it must be borne in mind that as soon as we enter the liquid region the  $pv$  term of the characteristic equation becomes the small difference of



two terms, a small percentage error in either of which becomes a large one in *pv*. The fact that the above table brings out is that from  $150^{\circ}$  to  $195^{\circ}$  the relation between volume and temperature given by the equation is so accurate as to make only the small errors in pressure in the above table. But to show this more directly, we will now compare the volumes of the liquid under a pressure of 9 metres of mercury between  $0^{\circ}$  and  $100^{\circ}$ , as determined by Grimaldi (*Wied. Beibl.* x.) and as given by the equation. The specific gravity of ethyl oxide at  $0^{\circ}$  and under one atmosphere is taken as  $\cdot 7366$ .

TABLE XVI. ( $p=19\cdot 5$  metre.)

Temperature .....	$0^{\circ}$ .	$50^{\circ}$ .	$100^{\circ}$ .	$150^{\circ}$ .
Volume, experiment.....	1·355	1·469	1·630	1·9
„ calculated .....	1·354	1·467	1·633	1·9

This, taken in conjunction with Table XV., shows that the equation represents with a high degree of accuracy the expansion of liquid ethyl oxide right up to the critical volume. It is now to be tested as to its power to give compressibilities correctly. The next Table contains the calculated compressibilities of liquid ethyl oxide, and also the experimental as given by Amagat (*Ann. de Chim. et de Phys.* 5 sér. t. xi.), Avenarius (*Wied. Beibl.* ii.), and Grimaldi (*Wied. Beibl.* x.). Amagat's values had to be interpolated for comparison with the others.

TABLE XVII.

Compressibilities with metre of mercury as pressure-unit.

Temperature .....	$0^{\circ}$ .	$40^{\circ}$ .	$60^{\circ}$ .	$100^{\circ}$ .
Amagat .....	·000200	·000309	·000380	·000730
Avenarius .....	·000178	·000317	·000403	·000654
Grimaldi .....	·000207	·000316	·000407	·000632
Equation .....	·000183	·000300	·000392	·000710

The agreement here is again satisfactory, and we have now seen that our form, with only two constants in addition to those characteristic of the gaseous state, can give both the expansion and compression of the liquid at low pressures; but Amagat has measured these also at high pressures up to 2000 and 3000 atmos. (*Compt. Rend.* ciii. and cv.), and the following Table compares first his values of the mean coefficient of expansion between  $0^\circ$  and  $50^\circ$  at pressures from 76 up to 2280 metres with those given by the equation, and, second, his values of the mean compressibility at  $17^\circ 4$  and at pressures up to 1500 metres with those given by the equation. If  $v_1$  and  $v_2$  are the volumes at  $p_1$  and  $p_2$ , then the mean compressibility is taken as  $(v_1 - v_2)/v_1(p_2 - p_1)$ . The apparent compressibilities given by Amagat are converted to true values by adding  $\cdot 000002$ , which he has since given as the compressibility of glass.

TABLE XVIII.

## Mean Coefficient of Expansion at high pressures.

$p$ in metres ...	76.	380.	760.	1140.	1520.	1900.	2280.
Amagat .....	$\cdot 00170$	$\cdot 00112$	$\cdot 00091$	$\cdot 00077$	$\cdot 00070$	$\cdot 00063$	$\cdot 00056$
Equation .....	$\cdot 00170$	$\cdot 00101$	$\cdot 00076$	$\cdot 00066$	$\cdot 00056$	$\cdot 00050$	$\cdot 00047$

## Mean Compressibilities at high pressures.

$p$ in metres ...	76 to	114 to	366 to	654 to	933 to	1218 to	1500
Amagat .....	$\cdot 000208$	$\cdot 000143$	$\cdot 000112$	$\cdot 000086$	$\cdot 000070$	$\cdot 000062$	
Equation .....	$\cdot 000197$	$\cdot 000128$	$\cdot 000085$	$\cdot 000060$	$\cdot 000046$	$\cdot 000037$	

As regards expansion the equation goes fairly near to the truth; except at the lowest pressures, it gives coefficients somewhat smaller than the experimental, but it parallels closely the main phenomenon of the rapid diminution of the coefficient with rising pressure. But in the compressibilities there is an increasing divergence between experiment and equation with increasing pressure, although again the equation is true to the main fact of the rapid diminution of compressibility with increasing pressure. We may conclude from the last table that our equation holds within the limits of experi-

mental accuracy up to 760 metres ; beyond that it begins to fail. A simple empirical modification would adapt the form to the whole of Amagat's range, but as it stands it will be found good enough for our applications.

We will now consider briefly how this form applies to carbonic dioxide below the critical volume ; and the comparison is interesting, as it relates to temperatures both above and below the critical. The values of the constants are  $B=54$ ,  $\beta=.692$ .

TABLE XIX.

Carbonic Dioxide below critical volume.

Volume .....	1.526.	1.203.	1.115.	1.027.
70° C. { Pressure, exp.....	150	274		
"      calc. ...	152	266		
35° C. { Pressure, exp.....	69	126	187	320
"      calc. ...	69	120	184	320
18° C. { Pressure, exp.....	.....	.....	99	200
"      calc. ...	.....	.....	97	208

The agreement is within the limit of experimental error at the high pressures. Cailletet and Mathias have determined (*Compt. Rend.* cii.) the density of liquid  $\text{CO}_2$  at various temperatures under the pressure of saturation. Here is a comparison with a couple of their results :—

Temperature . . .	-34°.	0 .
Volume—Cailletet and Mathias .	.946	1.087
"      Equation . . . . .	.943	1.086

As far as compound gases are concerned, the applicability of the form for volumes below the critical has now been demonstrated in two typical cases. The elementary gases have now to be considered as to their behaviour below the critical volume. The data are again those furnished by Amagat (*Compt. Rend.* cvii. and *Phil. Mag.* Dec. 1888) on the compressibility of these gases between 760 and 2280 metres of mercury. Our study of these bodies above the critical volume has given us the knowledge that the internal virial term below  $k$  must be  $l/v$ , and the kinetic-energy term at the critical volume is  $3RT/2$ , and with these guides the complete form

required is soon found from the experimental numbers. It is

$$pv = \frac{3}{2} RT \left( 1 + b \frac{\frac{3}{2}k - v}{v - \beta} \right) - \frac{l}{v},$$

with the following values for the additional constants  $\beta$  and  $b$  :—

	$k$ .	$\beta$ .	$b$ .
Hydrogen . . .	12	4.3	.480
Nitrogen . . .	2.64	.81	.420
Oxygen . . .	1.78	.604	.4415
Methane . . .	[5.51]	[1.59]	[.447]

The approximate equality of the values of the constant  $b$  is worth noting. I have also reproduced here the values of  $k$  at the side of those for  $\beta$ , in order to point out that  $\beta$  is nearly  $k/3$  in each case. Amagat has not published data for methane at volumes below the critical region, but the numbers given in brackets for methane were obtained indirectly as explained below. These relations of  $\beta$  and  $b$  give our equation such a degree of simplicity as largely to establish the soundness of its form. The next Table shows the degree of accuracy with which it represents the experimental facts.

TABLE XX.—Oxygen at high pressures.

Volume .....	1.277.	1.097.	1.008.	.949.	.905.
15° C. { Pressure, exp.....	760	1140	1520	1900	2280
"    "    calc. ...	739	1141	1512	1893	2296

The agreement is quite as good for hydrogen and nitrogen.

By means of this equation we can calculate the volumes of a gramme of liquid nitrogen and oxygen at their boiling-points under a pressure of .76 metre, for comparison with Wroblewski and Olszewski's determinations of the same (*Compt. Rend.* cii.; *Wied. Beibl.* x.; and 'Nature,' April 1887).

	Oxygen.	Nitrogen.
Volume { Wroblewski . .	.85	{ 1.20
at -184° { Olszewski . .	.89	{ 1.13
{ Equation . .	.90	{ 1.26



The equation is seen to give the volumes of these two bodies at these low temperatures within the present limits of experimental accuracy, and accordingly it covers a range of 2000-metres pressure and almost the whole experimental range of temperature. In the case of methane, if we take Olszewski's value 2.41 for its volume at  $-164^\circ$ , and assume  $b$  is the mean of  $b$  for  $H_2$ ,  $N_2$ , and  $O_2$ , then we can calculate the value of  $\beta$  which is tabulated above.

To ethylene above the critical region we had to assign a special form intermediate between that for ordinary compounds and that for elements; so that we had better do likewise for its infracritical equation, which I have cast in the form

$$pv = (1 + \frac{4}{5}) RT \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{\frac{5}{4}k - v}{v - \beta} \right) - \frac{l}{v} \cdot \frac{k}{k + a},$$

with  $B = 56.5$ ,  $\beta = 1.53$ . For the elements we had  $v_c = 3k/2$ , for ordinary compounds  $v_c = 7k/6$ ; so that to make ethylene intermediate  $v_c$  is taken as  $5k/4$ , all these being of the general form  $(1 + 2n)/2n$ , with  $n = 1, 2, 3$ .

With the values of the constants  $B$  and  $\beta$  given above as derived from Amagat's results at high pressures, we can determine the density of liquid ethylene; at  $-21^\circ$  under saturation-pressure the density is .414, identical with the experimental value of Cailletet and Mathias (*Compt. Rend.* cii.).

It will be as well at this stage to extract clear from among the argumentative detail the most important results so far obtained.

First, in the elements the internal virial varies inversely as the volume over the whole experimental range.

Second, in compounds there is mathematical discontinuity in the value of the internal virial at volume  $k$ ; from volume  $k$  downwards the internal virial varies inversely as the volume: from the volume  $k$  upwards it tends towards variation inversely as the volume as the limiting law, the limiting constant being double that which holds below the volume  $k$ ; between the two limiting cases the internal virial of compounds varies inversely as  $(v + k)$ .

Third, a fact of the highest importance in connexion with the kinetic-energy or temperature term in the equation arrests

our attention, namely, that the coefficient of  $T$  in it, or the apparent rate of variation of the translatory kinetic energy with temperature at constant volume, attains near the critical volume double its value in the gaseous state, and below the critical region increases rapidly with diminishing volume (see column  $R_{ef}(v)$  in Table I.), becoming at ordinary liquid volumes as much as ten times as large (see coefficient of  $T$  in infracritical equation). Now the specific heat of liquids at constant volume, which is the rate of variation of the total energy with temperature, is rarely much more than twice that for their vapours. Hence we must seriously consider the interpretation to be put on the different terms of our equations.

5. *A short digression on the general interpretation of Clausius's Equation of the Virial.*—Returning to Clausius's theorem of the virial,

$$\frac{3}{2}pv = \Sigma \frac{1}{2}mV^2 - \frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma Rr,$$

we see that strictly the kinetic-energy term includes not only the energy of the motion of the molecules as wholes, but also that of the motion of their parts, and at the same time the internal virial includes the actions between the parts of the molecules as well as those between the molecules. Calling these actions the chemic force, we can write the theorem thus:

$$\frac{3}{2}pv = \text{the total kinetic energy} - \text{chemic virial} - \text{virial of molecular forces.}$$

Now in the usual treatment of the equation it is assumed that the chemic virial is equal to that part of the total kinetic energy which is due to the motion of the parts of the molecules relatively to their centres of mass, and neutralizes it in our equation, reducing it to

$$\frac{3}{2}pv = \text{translatory kinetic energy of molecules as wholes} \\ - \text{virial of molecular forces.}$$

But if we retain the full equation, and assume that the virial term we have been finding for various bodies is the true virial of the molecular forces, and includes none of the chemic virial, then the term usually regarded as the translatory kinetic

energy of the molecules as wholes is really the total kinetic energy minus the chemic virial.

Let  $E$  be the total kinetic energy of unit mass,  $V$  the virial of the chemic forces, and  $P$  their potential energy; then, above the critical volume,

$$E - V = \frac{3}{2} RT \left( 1 + \frac{2k}{v+k} \right)$$

and

$$\frac{\partial}{\partial T}(E - V) = \frac{3}{2} R \left( 1 + \frac{2k}{v+k} \right),$$

which in the limiting gaseous state becomes  $3R/2$ .

Also

$$\frac{\partial}{\partial T}(E - P) = K_v,$$

the specific heat at constant volume.

Below the critical volume,

$$E - V = \frac{3}{2} R'T \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta} \right),$$

$$\frac{\partial}{\partial T}(E - V) = \frac{3}{2} R' + \frac{3}{4} R' \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta};$$

and, again,

$$\frac{\partial}{\partial T}(E - P) = K_v.$$

Now we can calculate  $K_v$  from the experimental values of  $K_p$  by the relation

$$K_v = K_p - T \frac{\partial p}{\partial T} \frac{\partial v}{\partial T}.$$

Let us then make a comparison in the case of ethyl oxide, using E. Wiedemann's value  $\cdot 3725$  for  $K_p$  for the vapour at  $0^\circ$ , and Regnault's value  $\cdot 529$  for the liquid at  $0^\circ$ ; then, converting to ergs per degree C., we get

	Vapour at $0^\circ$ .	Liquid at $0^\circ$ .
$\frac{\partial}{\partial T}(E - V)$	$= 1 \cdot 68 \times 10^6$	$15 \cdot 3 \times 10^6$ ,
$K_v$ or $\frac{\partial}{\partial T}(E - P)$	$= 14 \cdot 4 \times 10^6$	$17 \cdot 9 \times 10^6$ .

Thus we see that while in the liquid  $\partial(E - V)/\partial T$  is nearly

equal to  $\partial(E-P)/\partial T$ , there is a great difference in the vapour :

$\partial(V-P)/\partial T = 12.7$  for the vapour and only 2.6 for the liquid. Or, while  $K_v$  is nearly the same in the two states,  $\partial(E-V)/\partial T$  has in the liquid state increased to nine times its value in the vaporous. We have here, therefore, an interesting opening into the regions of chemic force ; but meanwhile we must restrict ourselves to the question of molecular force at present in hand, calling attention, however, to the fact that our energy term in its two forms for elements and its two forms for compounds is well worthy of the closest study. It summarizes a lot of information about the internal dynamics of molecules—perhaps about the relations of matter and æther ; but these would need to be extracted by a special research on the term and its relation to our experimental knowledge of specific heat. It is worth mentioning here that Clausius's equation of the virial, as usually applied to molecular physics, takes no account of the mutual action of matter and æther—an action which we know must exist, from the radiation of heat by gases as well as by liquids and solids. According to ordinary views of the æther this may be neglected, on account of the smallness of the mass and of the specific heat of the æther ; but it is well to remember that we are neglecting it.

6. *Consideration of Van der Waals's generalization.*—We are now in a position to consider how far Van der Waals's generalization holds, namely :—If the volume, pressure, and temperature are measured for each substance in terms of the critical values as units, then one and the same law holds for all substances.

In the first place, we see from what has gone before that the same law cannot apply to both elements and compounds, nor can the alcohols and water follow the same law as regular compounds.

In the case of the elements and methane we have the critical volume, pressure, and temperature given in terms of  $R$ ,  $l$ , and  $k$  by three relations (see end of Section 2),

$$v_c = 3k/2, \quad p_c = \frac{4}{27} \frac{l}{k^2}, \quad T_c = \frac{16}{27} \frac{l}{Rk}.$$



Whence, in the supracritical equation replacing  $R$ ,  $l$ , and  $k$  by their values in terms of  $v_c$ ,  $p_c$ ,  $T_c$ , we get

$$\frac{pv}{p_c v_c} = \frac{8}{3} \frac{T}{T_c} \left( 1 + \frac{1}{\frac{3v}{v_c} - 1} \right) - \frac{3v_c}{v};$$

which shows that when the critical values are made the units in the measurements of the variables, one and the same law holds for the elements above the critical volume.

Below the critical volume we have

$$\frac{pv}{p_c v_c} = \frac{9}{16} \frac{T}{T_c} \left( 1 + b \frac{1 - \frac{v}{v_c}}{\frac{v}{v_c} - \frac{\beta}{v_c}} \right) - \frac{3v_c}{v}.$$

We have seen that  $b$  is nearly the same for these bodies and that  $\beta/v_c$  is approximately constant, so that below the critical volume the elements and methane all follow approximately the same law.

In the case of compounds, we have (see Section 4, at the beginning)

$$v_c = 7k/6, \quad p_c = \frac{36}{409} \frac{l}{k^2}, \quad T_c = \frac{120}{409} \frac{l}{Rk},$$

with which, eliminating  $R$ ,  $k$ , and  $l$  from the supracritical equation, we get

$$\frac{pv}{p_c v_c} = \frac{20}{7} \frac{T}{T_c} \left( 1 + \frac{2}{\frac{7}{6} \frac{v}{v_c} + 1} \right) - \frac{409}{42} \frac{1}{\frac{7}{6} \frac{v}{v_c} + 1}.$$

Hence, above the critical volume the compounds follow the same law among themselves.

In the same way, below the critical volume we get for compounds:—

$$\frac{pv}{p_c v_c} = \frac{20}{7} \cdot \frac{25}{13} \frac{T}{T_c} \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{1 - \frac{v}{v_c}}{\frac{v}{v_c} - \frac{\beta}{v_c}} \right) - \frac{409}{98} \frac{v_c}{v}.$$

One and the same law holds for compounds below the

critical volume only if  $B$  varies as the square root of the critical temperature, and if  $\beta$  is proportional to the critical volume : in the elements we have found the latter condition to hold approximately, and so we are prepared to find it do so for compounds. The following Table compares  $B$  with  $\sqrt{T_c}$  and  $\beta$  with  $k$ , which is  $6v_c/7$  for the five compounds for which we have as yet found  $k$ . The values of  $B$  and  $\beta$  for  $\text{NH}_3$  and  $\text{N}_2\text{O}$  were obtained from Andréeff's data for the expansion of these bodies as liquids (*Ann. Chem. Pharm.* ex.) and for  $\text{SO}_2$  from Jouk's (*Wied. Beibl.* vi.).

TABLE XXI.

	$k$ .	$\beta$ .	$k/\beta$ .	$B$ .	$B/\sqrt{T_c}$ .
$(\text{C}_2\text{H}_5)_2\text{O}$ .....	4.066	1.11	3.7	63	2.9
$\text{CO}_2$ .....	1.76	.69	4.0	54	3.0
$\text{SO}_2$ .....	2.08	.55	3.8	71	3.6
$\text{NH}_3$ .....	4.8	1.22	3.9	70	3.6
$\text{N}_2\text{O}$ .....	2.3	.66	3.5	55	3.1

In these bodies we find a fair approximation to proportionality between  $\beta$  and  $k$  on the one hand, and between  $B$  and  $\sqrt{T_c}$  on the other ; to the same degree of approximation Van der Waals's generalization can be applied to compounds below the critical volume (excluding of course such exceptional bodies as the alcohols and water).

The accurate statement of the generalization ought then to be as follows :—When the variables are expressed in terms of their critical values as units, then down to the critical point compound bodies with certain exceptions have all one and the same characteristic equation, but below the critical point they have closely similar but not identical equations.

It is a remarkable fact that Van der Waals should have been led to his valuable generalization by means of a form of equation which completely fails to apply to the substances which are the subject of the generalization. As a point in the history of this branch of molecular physics, it calls for mention

that Waterston, in the *Phil. Mag.* vol. xxxv. (1868), had practically discovered the generalization, and expressed it in its most striking aspects by means of several diagrams for a number of bodies; but the verbal expression of his results was so unsystematic, and withal so crabbed, that his work has been overlooked.

There is one typical application of the generalization which is of special importance—to the relation between pressure and temperature of saturation. If with the aid of our equations we trace the complete isothermals for temperatures below the critical, we shall get curves with the James Thomson double-bend as shown in Ramsay and Young's isothermals for ether (*Phil. Mag.* May 1887).

According to Maxwell's thermodynamical deduction, the pressure of saturation at a given temperature is that corresponding to the line of constant pressure which cuts off equal areas in the two bends, a result which Ramsay and Young verified by actual measurement on their curves.

Let  $v_3$  and  $v_1$  be the volumes of saturated vapour and liquid at pressure  $P$  and temperature  $T$ ; then Maxwell's principle gives us that the pressure of saturation is defined by the three equations:—

$$P(v_3 - v_1) = \int_{v_1}^{v_3} p dv,$$

$$Pv_3 = RT \left( 1 + \frac{2k}{v_3 + k} \right) - \frac{l}{v_3 + k},$$

$$Pv_1 = \frac{25}{13} RT \left( 1 + \frac{\sqrt{T}}{B} \frac{\frac{7}{6}k - v_1}{v_1 - \beta} \right) - \frac{l}{2v_1}.$$

$v_3$  is given in terms of  $P$  and  $T$  by a quadratic, and can therefore be eliminated from the integral when evaluated;  $v_1$  is given by a cubic, but as  $Pv_1$  can for practical purposes be put 0, a very close approximation to  $v_1$  can be obtained also from a quadratic. The resulting relation between  $P$  and  $T$ , which is the law of saturation, involves the constants  $R$ ,  $k$ ,  $l$ ,  $B$ , and  $\beta$ .

The actual evaluation of the integral would of course proceed in three stages, corresponding to the supra-, circa-,

and infracritical equations. The law of the integral in the first stage from  $v_3$  to  $7k/6$ , with critical values of the variables as units, would be the same for all compounds; and we have seen that the integral in the other two stages will follow approximately the same law in all cases. Hence if saturation pressures and temperatures are expressed in terms of the critical values, the law of their relation will be approximately the same for all regular compounds.

If this were an absolutely accurate relation, the best means of testing it would be to take Regnault's formula, with one exponential term,

$$\log p = a + b\alpha^t,$$

and by a simple recalculation from his values for  $a$ ,  $b$ , and  $\alpha$ , to cast it in the form

$$\log p/p_c = e + d\gamma^{T/T_c},$$

proving that the constants  $e$ ,  $d$ , and  $\gamma$  are approximately the same for all compounds. But the objection to this plan soon becomes obvious on trial, as the formula owes its empirical convenience to the power of adjustment amongst the constants; and the same difficulty would be experienced with any purely empirical equation.

Accordingly, to test this matter, I have thought it best to compare the pressures of a number of bodies at temperatures which are constant fractions of their critical temperatures, such as  $\cdot 6 T_c$ ,  $\cdot 7 T_c$ , and so on. The ratio of the pressure of any substance to the corresponding pressure of ethyl oxide ought to be approximately the same for that substance at all values of the fraction. Great uncertainty attends the measurement of critical pressures: an error of  $20^\circ$  in the critical temperature is not a large fraction of its value measured from absolute zero, but it makes a large difference in a saturation-pressure, and the critical pressure is the limiting saturation-pressure. In the subjoined Table the critical-pressure ratios are given for what they are worth in the column  $T_c$ .

This table makes it clear enough that, in applying Van der Waals's generalization below the critical volume, we have to do with a first approximation only. The curves for all these diverse bodies excepting  $\text{CS}_2$ , while not identical, would form



TABLE XXII.

Ratios of Saturation-Pressures at constant fractions of the critical temperature to the Saturation-Pressures of Ethyl Oxide at the same fractions of its critical temperature.

	T <sub>c</sub> .	Fractions of T <sub>c</sub> .						
		·6.	·65.	·7.	·75.	·8.	·9.	1·0.
Acetone .....	506	·87	·90	·92	·94	·95	...	1·4
Methyl oxide.....	404	1·7	1·5	1·4	1·4	...	...	...
SO <sub>2</sub> .....	428	1·7	1·7	1·7	1·7	1·7	...	2·2
NH <sub>3</sub> .....	404	2·6	2·6	2·5	2·5	2·5	2·4	3·2
H <sub>2</sub> S .....	373	...	3·6	3·2	2·8	2·6	...	2·6
CO <sub>2</sub> .....	305	...	...	...	...	1·8	1·7	2·1
N <sub>2</sub> O .....	308	...	...	...	...	2·4	1·8	2·1
CS <sub>2</sub> .....	548	3·1	2·7	2·3	2·1	...	...	2·1
COCl <sub>2</sub> .....	556	1·3	1·3	1·3	1·2	...	...	1·6
CHCl <sub>3</sub> .....	537	1·6	1·5	1·5	1·4	1·3	...	1·6
CH <sub>3</sub> Cl .....	404	1·7	1·5	1·4	1·4	...	...	2·1
C <sub>2</sub> H <sub>5</sub> Cl .....	456	1·4	1·4	1·3	1·2	1·2	...	1·5
C <sub>2</sub> H <sub>5</sub> Br .....	509	1·9	1·5	1·6	1·5	1·4	...	...
Benzene, C <sub>6</sub> H <sub>6</sub> ...	560	1·3	1·3	1·2	1·2	1·1	...	1·4

a compact bundle about a mean curve from which each body would have its own characteristic departure; and this is just what our study of B and  $\beta$  in Table XXI. should lead us to expect.

7. *Five Methods of finding the Virial Constant.*—The first method is that which we have already exhausted, namely, by means of extended enough observations of the compression and expansion of bodies in the gaseous state.

Second method: to obtain the virial constant  $l$  from one measure of the compressibility and of the expansibility at the same temperature of the body as a liquid.

Writing our infracritical equation thus,

$$p = \frac{RT}{v} \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} \right) - \frac{l}{2v^2},$$

$$\frac{\partial p}{\partial T} = \frac{R'}{v} + \frac{3}{2} \frac{R' \sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} = \frac{3}{2} \cdot \frac{l}{2v^2 T} - \frac{R'}{2v} + \frac{3}{2} \frac{p}{T}$$

But at ordinary low pressures the term  $p/T$  is a negligible part of this expression, and we can write

$$\frac{\partial p}{\partial T} = \frac{3}{4} \cdot \frac{l}{v^2 T} - \frac{R'}{2v}.$$

Now

$$\frac{\partial p}{\partial T} = -\frac{\partial v}{\partial p} / \frac{\partial v}{\partial p} = -\frac{v_0}{v} \cdot \frac{1}{v} \frac{\partial v}{\partial T} = \frac{v_0}{v} \cdot \frac{\alpha}{\mu},$$

where  $\alpha$  and  $\mu$  are the coefficients of expansion and the compressibility at  $T$  as usually defined.

$$\therefore \frac{3}{4} \cdot \frac{l}{v^2 T} - \frac{R'}{2v} = \frac{v_0}{v} \frac{\alpha}{\mu};$$

$$\therefore = \frac{4}{3} \left( v_0 \frac{\alpha}{\mu} + \frac{1}{2} R' \right) v T = \frac{4}{3} \left( v_0 \frac{\alpha}{\mu} + \frac{2}{5} R \right) v T.$$

In addition to giving us a value of  $l$ , this last equation gives a test as to whether the equation applies to a body or not, as the expression on the right-hand side is to be constant at all temperatures if  $\mu$  is measured at low pressures. But on account of the experimental difficulties hitherto met with in the measurement of  $\mu$ , the equation gives no very delicate test, although it might with the improvements in accuracy made within the last few years. In addition to ethyl oxide, the two substances for which we have measurements of both  $\alpha$  and  $\mu$  over the widest range of temperature are ethyl chloride, studied as to expansion by Drion and as to compression by Amagat, who has corrected Drion's coefficients of expansion for change of pressure, and pentane, studied by Amagat and Grimaldi. The following are the values of  $l$  calculated from the data at different temperatures for these two substances, with the megadyne taken as unit of force.

Temperature C. ...	0°.	11°.	13°.	20°.	40°.	60°.	80°.	100°.
C <sub>5</sub> H <sub>12</sub> (Grimaldi)...	8530	...	...	7430	7230	8000	8300	9250
C <sub>5</sub> H <sub>12</sub> (Amagat) ...	...	...	9200	...	...	...	...	9250
C <sub>2</sub> H <sub>5</sub> Cl .....	...	5820	...	...	...	5450	...	5270

This comparison has been made to show how, from measurements of liquid compressibility at present available, we can get only a fair idea of the value of  $l$ , but not an accurate measurement of it.

Amagat has determined the compressibility of several other liquids at different temperatures (*Ann. de Chim. et de Physique*, sér. 5, t. xi.) ; so have Pagliani and Palazzo (*Wied. Beibl.* ix.) and de Heen (*Wied. Beibl.* ix.), but their discussion would bring out nothing more than the above comparison has. De Heen's results would appear to make  $l$  diminish with rising temperature in every case ; but he measured his compressibilities in comparison with that of water at the same temperature, and to calculate their values used Pagliani and Vincentini's values for water (*Wied. Beibl.* viii.), which make the compressibility of water much more variable with temperature than Grassi's. If we used Grassi's values in de Heen's experiments,  $l$  would remain nearly constant. We will accordingly use the compressibility-method of calculating  $l$  subsequently, only to illustrate the general agreement of values derived from purely mechanical experiments with those found by the more accurate methods to which we now proceed. The values found by this second method are tabulated later on in Table XXIV.

Third method of finding the virial constant  $l$  : from the latent heat. If we differentiate with respect to  $T$  our equation for saturation-pressures (see Section 6),

$$P(v_3 - v_1) = \int_{v_1}^{v_3} p dv,$$

we get

$$\frac{dP}{dT}(v_3 - v_1) + P\left(\frac{dv_3}{dT} - \frac{dv_1}{dT}\right) = \int_{v_1}^{v_3} \frac{\partial p}{\partial T} dv + P\left(\frac{dv_3}{dT} - \frac{dv_1}{dT}\right);$$

$$\therefore \frac{dP}{dT}(v_3 - v_1) = \int_{v_1}^{v_3} \frac{\partial p}{\partial T} dv.$$

Now from thermodynamics we have the relation

$$J\lambda = (v_3 - v_1)T dP/dT,$$

where  $\lambda$  is the latent heat,

$$\therefore J\lambda = \int_{v_1}^{v_3} T \frac{\partial p}{\partial T} dv,$$

which of course could have been written down immediately, for if we write it in the form

$$J\lambda = \int_{v_1}^{v_3} \left( T \frac{\partial p}{\partial T} - p \right) dv + P v_3 - P v_1,$$

we remind ourselves that the latent heat of evaporation of a liquid is the heat supplied to neutralize a Thomson and Joule cooling effect.

We must evaluate the integral in three stages,

$$\int_{v_1}^{v_3} T \frac{\partial p}{\partial T} dv = \int_{k'}^{v_3} T \frac{\partial p}{\partial T} dv + \int_k^{k'} T \frac{\partial p}{\partial T} dv + \int_{v_1}^k T \frac{\partial p}{\partial T} dv,$$

using in each integral the equation that holds between its limits.

In the first,

$$pv = RT \left( 1 + \frac{2k}{v+k} \right) - \frac{l}{v+k},$$

$$\frac{\partial p}{\partial T} = \frac{R}{v} \left( 1 + \frac{2k}{v+k} \right),$$

$$T \frac{\partial p}{\partial T} = p + \frac{l}{v+k}.$$

In the second,

$$pv = RT \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} \right) - \frac{l}{v+k},$$

$$T \frac{\partial p}{\partial T} = \frac{3}{2} \left( p + \frac{l}{v(v+k)} \right) - \frac{R'T}{2v}.$$

In the third,

$$pv = RT \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} \right) - \frac{l}{2v^2},$$

$$T \frac{\partial p}{\partial T} = \frac{3}{2} \left( p + \frac{l}{2v^2} \right) - \frac{R'T}{2v}.$$

Hence

$$\begin{aligned} J\lambda = \int_{k'}^{v_3} \left( p + \frac{l}{v+k} \right) dv + \int_k^{k'} \left\{ \frac{3}{2} \left( p + \frac{l}{v+k} \right) + \frac{R'T}{2v} \right\} dv \\ + \int_{v_1}^k \left\{ \frac{3}{2} \left( p + \frac{l}{2v^2} \right) - \frac{R'T}{2v} \right\} dv \end{aligned}$$



$$\begin{aligned}
&= \int_{v_1}^{v_3} p dv + \frac{1}{2} \int_{v_1}^{k'} p dv + \int_k^{v_3} \frac{ldv}{v(v+k)} + \frac{1}{2} \int_k^{k'} \frac{ldv}{v(v+k)} \\
&\quad + \frac{3}{4} \int_{v_1}^k \frac{ldv}{v^2} - \frac{1}{2} \int_{v_1}^{k'} \frac{R'T dv}{v} \\
&= P(v_3 - v_1) + \frac{1}{2} \int_{v_1}^{k'} p dv + \frac{l}{k} \log \frac{2v_3}{v_3 + k} + \frac{l}{2k} \log \frac{2k'}{k' + k} \\
&\quad + \frac{3l}{4} \left( \frac{1}{v_1} - \frac{1}{k} \right) - \frac{R'T}{2} \log \frac{k'}{v_1}.
\end{aligned}$$

We must now evaluate the only integral that has been left unevaluated,

$$\begin{aligned}
\int_{v_1}^{k'} p dv &= \int_{v_1}^{k'} \frac{R'T}{v} \left( 1 + \frac{\sqrt{T}}{B} \frac{k' - v}{v - \beta} \right) dv - \int_k^{k'} \frac{ldv}{v(v+k)} - \int_{v_1}^k \frac{ldv}{2v^2} \\
&= R'T \log \frac{k'}{v_1} + \frac{R'T}{B} \sqrt{T} \left( \frac{k' - \beta}{\beta} \log \frac{k' - \beta}{v_1 - \beta} - \frac{k'}{\beta} \log \frac{k'}{v_1} \right) \\
&\quad - \frac{l}{k} \log \frac{2k'}{k' + k} - \frac{l}{2} \left( \frac{1}{v_1} - \frac{1}{k} \right).
\end{aligned}$$

These last expressions are the only ones that introduce  $B$  and  $\beta$  into the value of  $J\lambda$ , and it is desirable to remove these two constants. At low pressures we can neglect the  $pv$  term in the infracritical equation, and we get

$$\frac{R'T}{B} \sqrt{T} = \left( \frac{l}{2v_1} - R'T \right) \frac{v_1 - \beta}{k' - v_1};$$

removing  $B$  by means of this we get

$$\begin{aligned}
J\lambda &= P(v_3 - v_1) + \frac{l}{k} \log \frac{2v_3}{v_3 + k} + \frac{l}{2} \left( \frac{1}{v_1} - \frac{1}{k} \right) \\
&\quad + \frac{1}{2} \left( \frac{l}{2v_1} - R'T \right) \frac{v_1 - \beta}{k' - v_1} \left( \frac{k' - \beta}{\beta} \log \frac{k' - \beta}{v_1 - \beta} - \frac{k'}{\beta} \log \frac{k'}{v_1} \right).
\end{aligned}$$

We can now remove  $\beta$  and greatly simplify this equation, if we apply it to latent heats near the ordinary boiling-point  $T_b$ . The last term taken in its entirety has a small numerical value compared to the rest, so that in it we can make approximations without any sacrifice of accuracy worth considering: we have seen that  $\beta$  is approximately proportional to  $k$  (see Table XXI.) and  $v_1$ , the volume of the liquid at the boiling-

point, may be assumed to be approximately proportional to  $k'$  the volume at the critical temperature, and  $k'=7k/6$ : hence the coefficient of  $(l/2v_1-R/T)$  in the last term is approximately the same for all bodies and we can evaluate it for ethyl oxide; call it  $C$ . Again, in  $P(v_3-v_1)$  neglect  $v_1$  and assume the gaseous law  $Pv_3=RT_b$ . And further,  $k$  is small compared to  $v_3$ , so that  $2v_3/(v_3+k)$  is nearly 2, and its value for ethyl oxide can be applied to all bodies.  $R'=25R/13$ . Hence multiplying by  $M$  the molecular weight we can write

$$\frac{Ml}{k} \left\{ \frac{1}{2} \left( \frac{k}{v_1} - 1 \right) + \log \frac{2v_3}{v_3+k} + \frac{C}{2} \frac{k}{v_1} \right\} = JM\lambda + MR \left( \frac{25}{13} C - 1 \right) T_b.$$

$MR$  is the same for all bodies, and  $T_b$  is the absolute boiling-point. This equation still involves  $k$  as well as  $l$ ; when  $k$  is not known we must eliminate it by means of our previous assumption, namely, that  $k$  is proportional to  $v_1$ , which we know to be approximately true; in so far as it is inexact it will introduce inexactness into our calculation of  $l$ . Accordingly in symbols  $k/v_1=r$ , where  $r$  is the same for all bodies, and can be found for ethyl oxide. Making the numerical reductions we get

$$Ml/v_1 = 66.5 M\lambda - 101 T_b$$

as the equation which gives  $l$  in terms of the megadyne as unit of force, when  $\lambda$  is the latent heat of a gramme in calories and  $v_1$  its volume in cubic centimetres at the absolute boiling-point  $T_b$ . This equation will be abundantly verified afterwards in Table XXIV.; but meanwhile, if to test it we apply it to calculate the latent heat of ethyl oxide, we find  $\lambda=83.4$ , whereas several experimenters have agreed in an estimate of about 90; but, on the other hand, Ramsay and Young (Phil. Trans. 1887) have made a special study of the terms in the thermodynamic relation  $J\lambda=(v_3-v_1)TdP/dT$ , and have so calculated values of  $\lambda$  almost up to the critical temperatures, their value at the boiling-point is 84.4, and there is the same amount of discrepancy between their values at higher temperatures and Regnault's experimental determinations. Yet Perot, who has made an elaborate study (*Ann. de Ch. et de Ph.* sér. 6, t. xiii.) both of  $\lambda$  experimentally

and of the quantities involved in its calculation by the thermodynamic relation, has found the most perfect harmony between the results of the two methods. Now at  $30^{\circ}\text{C}$ . Perot gives as the saturation-volume of the vapour 400.4, and the saturation-pressure .635 metre, while Ramsay and Young's values are 374 and .648 metre; but if ethyl oxide were a perfect gas, under Perot's pressure of .635 metre it would have a volume of 400.8, almost identical with his value: yet we cannot imagine that ethyl oxide under this pressure and at this temperature is so nearly a perfect gas as this would imply, unless there is some remarkable discontinuity in its behaviour at high volumes. Accordingly, in spite of the thoroughness of the researches of both Perot and Ramsay and Young, we are on the horns of a triple dilemma, from which only some experimental repetition can deliver us, and demonstrate where the cause of these discrepancies lies. Wüllner and Grotrian (*Wied. Ann.* xi.) have put on record the results of experiments which indicate the cause; they find the pressure of condensation measurably different from the ordinarily measured saturation-pressure,—a fact explaining the difficulty of measuring  $v_3$  accurately, and showing also that the values of  $dP/dT$  are not so reliable as usually supposed.

Our last equation is verified by, and shows us the cause of, an interesting relation that has been independently discovered and expressed in different forms, between the molecular latent heat and the boiling-point, by Pictet (*Ann. de Ch. et de Ph.* sér. 5, t. ix. 1876), Trouton (*Phil. Mag.* xviii. 1884), and Ramsay and Young (*Phil. Mag.* xx. 1885), namely, that the molecular latent heats of fluids are nearly proportional to their absolute boiling-points. Now we have seen that  $T_c = 120l/409Rk$  (Section 4), and I have noticed that a large number of substances have their ordinary absolute boiling-points nearly equal to  $2T_c/3$ , and  $k$  is nearly proportional to  $v_1$ , say is equal to  $2.8v_1$ , as it is for ethyl oxide. Hence we have

$$\frac{3}{2}T = \frac{120l}{409R \cdot 2.8v_1};$$

$$\therefore Ml = 14.3MRv_1T_b = 1190v_1T_b,$$

when the megadyne is the unit of force; hence from our equation for  $Ml$  in terms of  $\lambda$  we have

$$1190T_b = 66.5 M\lambda - 101 T_b ;$$

$$\therefore 1291 T_b = 66.5 M\lambda \quad \text{or} \quad M\lambda = 19.4 T_b,$$

or the molecular latent heat is proportional to the absolute boiling-point.

(It is to be noted that  $Ml = 1190 v_1 T_b$  gives a rough means of obtaining  $l$  from the boiling-points and the volumes at the boiling-points of liquids, which might be convenient when better data are wanting.)

Robert Schiff (*Ann. der Chem.* ccxxxiv.) has made the most accurate determinations to test this relation between molecular latent heat and boiling-point. For 29 compounds of the form  $C_n H_{2n} O_2$ , from ethyl formiate up to isoamyl valerate, he finds  $M\lambda = 20.8 T_b$  in the mean, the greatest departures being 20.4 for propyl isobutyrate, and 21.1 for propyl formiate; for 8 hydrocarbons of the benzene series he finds a mean coefficient 20, with 19.8 for cymene and 20.6 for benzene as the greatest departures. To these 37 examples we will add the following from Trouton's paper, doubling his numbers, as he used density instead of  $M$ .

TABLE XXIII.—Values of  $M\lambda/T_b$ .

$C_2H_5Cl.$	$CHCl_3.$	$CCl_4.$	$AsCl_3.$	$SnCl_4.$	$SO_2.$	$CS_2.$
21	22	21	21	20	23	21
$(C_2H_5)_2O.$	$(C_5H_{11})_2O.$	$(CH_3)_2CO.$	$C_{10}H_{16}.$	$(C_2H_5)_2C_2O_4.$		
22	24	23	22	23		

The mean value of the coefficient is higher than that deduced theoretically above (19.4), because in round fraction we wrote  $T_b = 2T_c/3$ , but the general truth of the relation is well enough brought out.



Fourth method of finding the virial constant  $l$ : from the critical temperature and pressure. Now we have (Section 4),

$$T_c = 120l/409Rk, \quad p_c = 36l/409k^2,$$

$$\therefore T_c/p_c = 10k/3R \quad \text{and} \quad l = 409R^2T_c^2/400p_c,$$

this is for compounds; for elements  $l = 27R^2T_c^2/64p_c$ . Where both the critical pressure and temperature are known, this gives  $l$  theoretically with accuracy, but practically the difficulties in measuring the critical pressure introduce inaccuracy. In the relation  $T_c/p_c = 10k/3R$ , as  $R$  varies inversely as the molecular weight, we see that the molecular domains (Molecular volumes) of bodies at the critical temperature are proportional to the quotient of critical temperature by critical pressure, a relation which Dewar has proved experimentally (Phil. Mag. xviii. 1884) for 21 volatile bodies, for which he has determined and collected the data. These with other data since published enable us to determine values of  $l$  for certain bodies for which the other methods are not available.

As there are many more critical temperatures determined up to the present than critical pressures, and as we have seen that an error in the critical temperature is of less relative importance than an error in the critical pressure, we can make ourselves independent of critical pressures with advantage, by employing the approximation that has already been useful to us, that  $k$  is proportional to the volume of the liquid at the boiling-point or  $k = 2.83v_1$ . Then

$$Ml = 409MRT_c k/120 = 800T_c v_1$$

approximately, with the megadyne as unit of force. This is a more accurate form of the relation  $Ml = 1190T_b v_1$  given above, in which we assumed the approximation  $T_b = 2T_c/3$ .

8. *Fifth or Capillary Method of finding the Internal Virial Constant*, with digressions on the Brownian movement in liquids and on molecular distances.—So far we have been proceeding on a purely inductive path, with two deductive guides in Clausius's equation of the virial and in the law of the inverse fourth power, which requires that the internal virial should vary inversely as the volume. But now, in passing on to our fifth and most useful method of finding  $l$

from surface-tension, we must employ a deductive relation between  $l$  and surface-tension, furnished by the law of the inverse fourth power. In a previous paper (Phil. Mag. July 1887) it was shown that if the law of force between two molecules of mass  $m$ , at distance  $r$  apart is  $3Am^2/r^4$ , then the internal virial for the molecules in unit mass is  $3\pi A\rho \log L/a$ ,  $\rho$  being density, and  $L$  a finite length of the order of magnitude of the linear dimensions of the vessels used in physical measurements,  $a$  being the mean distance apart of the molecules. The ratio  $L/a$  remains the same for a given mass whatever volume it occupies, but I also assumed that  $L/a$  is so large a number that  $\log L/a$  would hardly be affected by such large variations as might occur in the value of  $L$  when the behaviour of a kilogramme of a substance was compared with that of a milligramme. To remove the haziness of this assumption, I will now make a more accurate evaluation of the internal virial.

By definition it is  $\frac{1}{2} \cdot \frac{1}{2} \cdot \Sigma \Sigma 3Am^2/r^3$ , and we will evaluate it for a spherical mass. To cast it into the form of an integral, take any molecule  $m$  amongst the number  $n$  in a spherical vessel of radius  $R$ ; gather it to its centre as a true particle and spread the remaining  $n-1$  in a uniform continuous mass separated from  $m$  by a small spherical vacuum of radius  $a$ , so chosen that the virial of  $m$  and the continuous mass is the same as that of  $m$  and the  $n-1$  molecules.

Suppose  $m$  at the point  $O$ , and the centre of the vessel at  $C$ , and let  $OC=c$ . Take  $OC$  as axis of  $x$  and any two rectangular axes through  $O$  as axes of  $y$  and  $z$ . Let polar coordinates  $r \theta \phi$  be related to these in the usual manner. Then the equation to the surface of the sphere is

$$(x-c)^2 + y^2 + z^2 = R^2 \quad \text{or} \quad r^2 - 2cr \sin \theta \cos \phi + c^2 - R^2 = 0.$$

Let  $r_1$  and  $r_2$  be the two roots of this equation in  $r$  so that  $r_1 r_2 = R^2 - c^2$ . Then  $m^2/r^3$  can be replaced by

$$mpr^2 \sin \theta d\theta d\phi dr/r^3,$$

and

$$\Sigma m^2/r^3 \text{ by } \iiint mp \sin \theta d\theta d\phi dr/r.$$

If we integrate with respect to  $r$  on one side of the plane  $yz$  from  $a$  to  $r_1$  and on the other from  $a$  to  $r_2$  and add the two results,

then we have to take  $\theta$  and  $\phi$  each between 0 and  $\pi$ , thus :

$$\Sigma m^2/r^3 = \int_0^\pi \int_0^\pi m\rho \sin \theta d\theta d\phi \left[ \int_a^{r_1} dr/r + \int_a^{r_2} dr/r \right].$$

The two integrals in brackets give

$$\log r_1 r_2 / a^2 = \log (R^2 - c^2) / a^2.$$

Hence

$$\Sigma m^2/r^3 = 2\pi m\rho \log (R^2 + c^2)/a^2.$$

To perform the second summation we can first add the values of the last expression for all the molecules at distance  $c$  from the centre of the vessel, and write the result in the form

$$2\pi\rho 4\pi\rho c^2 dc \log (R^2 - c^2)/a^2,$$

and we then have

$$\frac{1}{2} \cdot \frac{1}{2} \Sigma \Sigma 3A m^2/r^3 = 6A\pi^2\rho^2 \int_0^{R-a} c^2 dc \log (R^2 - c^2)/a^2.$$

Evaluating the integral, this becomes

$$6A\pi^2\rho^2 \left\{ \frac{1}{3} (R-a)^3 \log \frac{2R-a}{a} - \frac{2}{9} (R-a)^3 - \frac{2}{3} R^2 (R-a) + \frac{R^3}{3} \log \frac{2R+a}{a} \right\},$$

in which, neglecting unity in comparison with the large number  $R/a$ , we get

$$A\pi^2\rho^2 R^3 \{4 \log 2R/a - 16/3\}.$$

But if  $W$  is the total mass in the vessel, then

$$W = 4\pi r^3 \rho / 3,$$

and we get

$$W a \pi \rho \{3 \log 2R/a - 4\}.$$

When  $W=1$  the first term of this becomes identical with the value of the internal virial previously given, with  $2R$  written instead of  $L$ . Replacing  $R$  by its value in terms of  $W$  and  $\rho$ , we get for the internal virial of mass  $W$ ,

$$W A \pi \rho (\log 6W/\pi \rho a^3 - 4).$$

As  $\rho a^3$  is constant, we see that for a given mass the internal virial for molecular force varying inversely as the fourth power is rigorously proportional to the density, but it is not purely proportional to the mass. Although the number  $6W/\pi \rho a^3$  is a large one, and has a logarithm varying slowly with  $W$ , yet large enough variations in  $W$  can affect it

appreciably, as we see if provisionally we accept Sir W. Thomson's estimate of  $2 \times 10^{-9}$  centim. as the lowest possible value for  $\alpha$ . Suppose  $\pi\rho=3$ , then  $6W/\pi\rho\alpha^3$  is  $10^{27}W/4$ , and if  $W$  is 4000, 4, or .004 grm., then the values of  $\log 6W/\pi\rho\alpha^3$  are as 30, 27, and 24, and we have a larger mass variation of the internal virial than is likely to have escaped detection in its effects, such as a difference in the density, expansion, compressibility, latent heat, and saturation-pressures of a liquid as measured on a milligramme, from their values as measured on a kilogramme. The raising of this difficulty suggests to us in passing that there exists a department of microphysics in which little has as yet been done by the experimenter, and that great interest would attach to a research determining when a mass variation of the properties usually spoken of as physical constants actually sets in.

But meanwhile we must scrutinize more closely the meaning of our last result. According to the views of Laplace (and of the early elasticians), if a plane be drawn dividing a mass of solid or liquid into two parts, then, in consequence of molecular force, the one part exercises a resultant attraction on the other, and this has to be statically equilibrated by a pressure (called the molecular or internal pressure) acting across the plane, a conception which is necessary in any purely statical theory of elasticity. Adopting for the moment this mode of viewing things, we see that our result amounts to this, that the internal pressure is measurably greater at the centre of a kilogramme than of a milligramme.

But if we try to carry out the kinetic theory in its integrity, we must reject the idea of a statical pressure, and replace it by its kinetic equivalent of a to and fro transfer of momentum; this may take place as a quite indiscriminate traffic of individual molecules across the plane, or as such a traffic modified by the existence of streams of molecules in opposite directions. If streams, or motions of molecules in swarms, actually exist in fluids, then our interpretation of the equation of the virial would have to take account of their existence. The kinetic energy of the motion of a swarm as a whole would not count as heat but as mechanical energy, and for the amount of it we should have approximately the kinetic energy of the swarm motion equal to the virial of the forces between the swarms.



Therefore we require to divide the energy into two parts, that of molecular motion inside the swarm constituting heat and that of the swarm ; in the same way the internal virial is divided into two parts, one within each swarm, the other between the swarms. But the swarms could on the average be regarded as equivalent to spheres of radius  $L$ , where  $L$  must be supposed nearly independent of mass and liable to the same variations with temperature and pressure as the linear dimensions of any quantity of the liquid, so that  $L$  is proportional to  $a$ , and our expression (theoretical)  $WA\pi\rho(3\log 2L/a-4)$  for the internal virial becomes purely proportional to the mass and purely proportional to the density, as  $3Wl/4v$  our experimental internal virial for a mass  $W$  of a compound liquid is.

This hypothesis would affect somewhat the rigorousness of certain thermodynamical relations as usually interpreted, such as  $J\lambda = (v_3 - v_1)Td\rho/dT$ , since it provides a supply of internal mechanical energy not taken account of ; but if this supply is only slightly variable with pressure and temperature it would make little difference in most parts of thermodynamics.

With the addition of this hypothesis of molecular swarms, which will be used only in calculating molecular distances, and will not affect at all the rest of our work, the law of the inverse fourth power is brought into strict harmony with the behaviour of compound liquids and of elements both as liquids and gases. We must therefore inquire what experimental evidence there is for the existence in liquids of a motion of swarms of molecules, possessing the remarkable property of not being degraded to heat as ordinary visible motions are. In the motion long familiar to microscopists as the Brownian movement we have such evidence. Gouy has recently (*Compt. Rend.* cix. p. 103) recalled the attention of physicists to this remarkable ceaseless motion of granules in liquids. He states that it occurs with all sorts of granules, and with an intensity less as the liquid is more viscous and as the granules are larger. It occurs when every precaution is taken to ensure constant temperature, and to ensure the absence of all external causes of motion. Granules of the same size but as different in character as solid granules, liquid globules, and gaseous bubbles, show but little difference in their motions—a

fact which proves that the cause is to be looked for not in the granules themselves but in the liquid, the granules being merely an index of motions existing in the liquid. The most pronounced character of the motion is its rapid increase with diminishing size of granules, so that all that is seen under the microscope is the limit of movements of unknown magnitude. Gouy considers the Brownian movements to be a remote result of the motion of the molecules themselves, but according to what we know of molecular dimensions I fancy that the Brownian movement must be considered rather as a sign of the motion of swarms of molecules. If swarms of molecules are weaving in and out amongst one another, so that the average transfer of momentum at a point is the same in all directions, then the vibratory agitation of granules amongst the swarms is just what we should expect. The striking fact about the Brownian movement is that it is ceaseless; it is never degraded into heat. This alone forces us to conceive a form of motion existing in liquids on a larger scale than molecular motion but possessing its character of permanence; in other words, the motion of swarms of molecules.

The existence of swarms would not affect our views of the rise of liquids in capillary tubes as a purely statical question; so that, for the connexion between molecular force and surface-tension, we can use the calculation given in another paper (*Phil. Mag.* April 1889) (rather badly affected with misprints), where I have shown that the surface-tension of liquids that wet glass, measured in tubes so narrow that the meniscus-surface is a hemisphere, is given by the equation

$$\alpha = \pi \bar{\rho}^2 A e / (2 + \sqrt{2}) ;$$

where  $\rho$  is the average density of the capillary surface-film (to be written also  $1/v$ ), and  $e$  is the distance which we must suppose to be left between a continuous meniscus and the base of a continuous column raised by its attraction, if the action between the continuous distributions is to be the same as in the natural case of discontinuous molecular constitution of meniscus and column. The distance  $e$  is not identical with the length  $a$  which occurs in our theoretical value of the internal virial of unit mass,

$$A\pi\rho(3\log 2L/a - 4) = \frac{3}{2} \frac{l}{2v},$$

but it is closely proportional to it. If we can find the relation between  $e$  and  $a$ , then from capillary determinations we can obtain relative values of the virial constant  $l$  which, as we have already found some absolute values of  $l$ , can be converted to absolute values; at the same time, too, we shall be able to find a value of  $a$  the mean distance apart of the molecules.

To find the relations between  $e$  and  $a$  we can proceed thus. If we have a single infinite straight row of molecules at a distance  $a$  apart, the force exerted by one half of it on the other is

$$\sum_{n=0}^{\infty} \sum_{p=1}^{\infty} \frac{3Am^2}{(p+n)^4 a^4},$$

which can easily be evaluated as approximately  $3.6Am^2/a^4$ . Two infinite continuous lines in the same line, of density  $m/a$  with distance  $e$  between their contiguous ends, would exert a force

$$\frac{3Am^2}{a^2} \int_e^{\infty} \int_0^{\infty} \frac{dx dy}{(x+y)^4}$$

on one another; this is equal to  $Am^2/2a^2e^2$ . If, then, the continuous distribution is to be equal to the molecular, we have

$$e^2 = a^2/7.2, \quad e = a/2.7.$$

Again, if along two infinite axes one at right angles to the other and terminating in an origin O at its middle point molecules are arranged along each at distance  $a$  apart starting from O, then the force exerted by the unlimited row on the other is

$$2 \sum_{p=1}^{\infty} \sum_{n=1}^{\infty} \frac{3Am^2 n}{(p^2 + n^2)^{\frac{5}{2}} a^4} + \sum_{p=1}^{\infty} \frac{3Am^2}{p^4 a^4},$$

which can be evaluated at about  $5Am^2/a^4$ .

Replace the rows by two continuous line-distributions of density  $m/a$ , the one terminating at a distance  $e$  from O: it is required to find  $e$  so that the force may be the same as this. The force is

$$\frac{6Am^2}{a^2} \int_e^{\infty} \int_0^{\infty} \frac{y dy dx}{(x^2 + y^2)^{\frac{5}{2}}} = Am^2/a^2 e^2.$$

Hence in this case

$$e^2 = a^2/5, \quad e = a/2.2.$$

From these two simple cases we get an idea of the relation between  $e$  and  $a$ . The case of a meniscus attracting the column which it raises in a capillary tube is more analogous to the second than to the first, and it is easy to see that in the case of the meniscus we can say that  $e$  is not less than  $a/2.2$ . It will suffice to write  $e = a/2.2$ .

Now according to the definition of  $a$  in our theoretical expression for the internal virial, it is the radius of the spherical vacuum artificially used to represent the domain of a molecule; but as it occurs in the expression  $\log 2L/a$ , where  $2L/a$  is a very large number and the value of  $L$  is indefinite, we see that there is no inaccuracy in making it identical with  $a$  the mean distance apart of the molecules. However, for the sake of formal completeness, we can easily find the relation between the two quantities which we have denoted by the one symbol  $a$ . Let us now denote by  $x$  the mean distance apart of the molecules, that is the edge of the cube in a cubical distribution of the molecules; then, from the definition of  $a$ ,  $x$  and  $a$  are connected by the relation

$$\Sigma A m^2 / r^3 = \int_a^R 4\pi A m^2 dr / x^3 r,$$

the summation being extended to all the molecules in a sphere of radius  $R$ . By actual summation up to  $R = 5x$  we find approximately  $a = .9x$ .

With our previous estimate of  $e$  as  $a/2.2$ , which we must now write  $x/2.2$  on account of our change of symbol for mean distance apart, we have the two equations,

$$l = A\pi(4 \log 2L/.9x - 16/3),$$

$$\alpha = \pi \bar{\rho}^2 A x / 2.2 (2 + \sqrt{2}).$$

We can replace  $\bar{\rho}$  by  $\rho$ , the difference between them being necessarily very slight. Then for ethyl oxide we have the following data:  $\alpha$  at the boiling-point according to Schiff is 1.57 grammes weight per metre, or  $1.57/10^5$  kilog. per cm.;

$l$  is 7500 kilog. cm.<sup>4</sup>, and  $v_1 = 1.44$  cm.<sup>3</sup> Eliminating  $A$  from the two equations, we have a relation between  $x$  and  $L$ , namely

$$x = 7.5 v_1^{\frac{2}{3}} \frac{\alpha}{l} (9.2 \log_{10} 2L/.9x - 16/3).$$

$L$  being hypothetical is not known to us, but we can give it a series of possible values, and calculate by trial from the last equation the corresponding series of values for  $x$ , with the following results:—

$L$ .	$x$ .
$1/10^5$ cm.	$4.6/10^7$ cm.
$1/10^4$ „	7.7 „ „
$1/10^3$ „	11.0 „ „

As it is subsequently to be shown that in liquid ethyl oxide and in all regular compound liquids the molecules are paired, and that each pair acts on the others as if it were a single molecule, we may estimate it as likely that the mean distance apart of the pairs in ethyl oxide is between 1 and 10 micromillimetres ( $1/10^6$  mm.). This result, though 100 times as large as Sir William Thomson's limits for the distance apart of molecules in liquids, namely  $2 \times 10^{-9}$  cm. and  $7 \times 10^{-9}$  cm., is yet in better agreement with the estimate of molecular distances arrived at by Rücker (Journ. Chem. Soc. 1888) as the most probable result obtainable from the most important attempts yet made to measure the range of molecular forces. The most suggestive of these is Reinold and Rücker's discovery, that the equilibrium of a soap-solution film becomes unstable when its thickness is reduced to between 96 and 45 micromillimetres, but again becomes stable when the thickness is still further reduced to 12 micromillimetres. At the latter thickness the film shows black in reflected light. If the intermolecular distances are nearly the same in soap-solutions as in liquid ethyl oxide, then the black film must be regarded as consisting of a single layer of molecules or groups of molecules (in the case of water the molecules will subsequently be shown to go in double pairs). This is an intelligible result, and gives the simplest explanation of Reinold and Rücker's beautiful discovery of a stable thickness supervening on the



unstable, for we recognize a single layer of molecules as a stable configuration. Of course it is to be understood that what we mean by the thickness of a single layer of molecules is the one  $n$ th part of the thickness of  $n$  layers; and if the black film is really only a single layer, it is in this sense that Reinold and Rücker's estimate of 12 micromms. is to be taken, for they did not measure an actual distance from the front to the back of a black film, but only estimated from accurate and accordant measurements, made in entirely different manners, that the number of layers in the black film is to the number in a thickness of 1 centim. as 12 micromms. is to 1 centim.

If the black film consists really of only a single layer of molecules, it is surely a hopeful sign for molecular physics that measurements should have been possible on it, though only visible through its invisibility.

If, encouraged by this experimental support, we say that in round numbers the mean distance between the pairs of molecules in liquid ethyl oxide is 10 micromms., then one gramme contains  $2v_1 \times 10^{18}$  molecules, or the mass of a single molecule is

$$1/2.88 \times 10^{18} \text{ grm.} = 3.5/10^{19},$$

and so the mass of an atom of H is

$$3.5/74 \times 10^{19} = 5/10^{21} \text{ grm. nearly.}$$

It would lead us too far from our present purpose to discuss other estimates of molecular distance, especially as Reinold and Rücker's measurement of the black film is the most definite and striking yet made of these minute distances; but the question of the range of molecular force is of special importance to us.

Quincke (*Pogg. Ann.* cxxxvii.) determined what thickness of silver it is necessary to deposit on glass so that the capillary effect on water may be the same as that of solid silver; that is, at what distance the difference between the molecular attractions of glass and silver for water becomes too small to be measured. He found the thickness to be about 50 micromms.

Now, according to the law of the inverse fourth power, the attraction of a cylinder of radius  $c$ , length  $h$ , and density  $\rho$  on

a particle of mass  $m$  on the axis at a distance  $z$  from the nearest end is easily calculated as

$$2A_m\rho\pi\left(\frac{1}{z}-\frac{1}{z+h}-\frac{1}{\sqrt{c^2+z^2}}+\frac{1}{\sqrt{c^2+(z+h)^2}}\right).$$

If the cylinder consists of a length  $h_1$  of silver with a length  $h_2$  of glass, the silver being near the particle, then, the suffixes 1 and 2 applying to silver and glass, the attraction of the composite cylinder is

$$2A_1m\rho_1\frac{\pi}{z}-2m\pi(A_1\rho_1-A_2\rho_2)\left(\frac{1}{z+h_1}-\frac{1}{\sqrt{c^2+(z+h_1)^2}}\right) \\ -2A_1m\rho_1\frac{\pi}{\sqrt{c^2+z^2}}-2A_2m\rho_2\pi\left(\frac{1}{z+h_1+h_2}-\frac{1}{\sqrt{c^2+(z+h_1+h_2)^2}}\right).$$

Making the circumstances correspond to Quincke's experiment, we have  $z$  nearly equal to the mean molecular distance in water, about 10 micromms.;  $h_1$  is small compared to  $h_2$  and  $c$ , and, according to Quincke, is 50 micromms. when the composite cylinder exerts the same force on  $m$  as if it were all silver; accordingly the last expression reduces to the two terms

$$2A_1m\rho_1\pi/z-2m\pi(A_1\rho_1-A_2\rho_2)/(z+h_1),$$

which permit us to compare the molecular force range  $h_1$  with the molecular distance  $z$ . That the second of these terms should become negligible when  $h_1$  is 50 micromms. is a result quite in accordance with the value 10 micromms. for  $z$ .

Let us briefly compare the magnitudes of molecular and gravitational force. The most convenient plan will be to compare the two forces in the case of two single ethyl-oxide molecules at a distance of one centim. apart; that is, to calculate  $Am^2$  and  $Gm^2$ , where  $m$  is the actual mass of the molecule, and  $G$  the constant in the expression  $Gm^2/r^2$  for gravitation.

In the expression

$$\alpha=\pi\bar{\rho}^2Ax/2\cdot2(2+\sqrt{2}),$$

using the value 10 micromms. for  $x$  and the values previously

given for the other quantities, we can find  $A$ , and then using the value  $3.5/10^{19}$  for the mass of a molecule of ethyl oxide we find  $Am^2 = 9/10^{30}$  in terms of the dyne. To calculate  $G$  we have 981 as the acceleration of gravitation; the mass of the earth is  $6 \times 10^9$  gramm. and its radius is  $6.37 \times 10^7$  cm., so that  $Gm^2 = 2.1/10^{29}$  in terms of the dyne. Hence at a distance of 1 centim. the gravitation of two ethyl-oxide molecules is about double their molecular attraction, or, allowing for uncertainties in our calculation, we may say that at about 1 centim. apart two molecules exert the same gravitational as molecular force on one another.

We now return to the main business of this section, which is the *Fifth Method* of finding the virial constant  $l$ . This consists in using the equation already used for calculating molecular distances in the form

$$l = 7.5v^2\alpha(4 \log 2L/9x - 16/3)/x.$$

Now  $x$ , the molecular distance for different liquids, varies as  $m^{\frac{1}{3}}v^{\frac{1}{3}}$ , and the expression in brackets may be assumed to be the same for all bodies; hence  $l = cav^{\frac{2}{3}}/m^{\frac{1}{3}}$ , where  $c$  is a constant whose value can be obtained on substituting in the case of ethyl oxide the known values of  $l$ ,  $\alpha$ ,  $v$ , and  $m$ , or, more safely, by taking a mean value from several substances.

But we must remember that we are using  $v$  the volume in the body of the liquid, instead of  $\bar{v}$  that in the surface-film; a replacement which is not justified by experiment, seeing that for a given liquid  $\alpha v^{\frac{2}{3}}$  measured at different temperatures is not constant, the reason being that  $v$  varies much more rapidly with temperature than  $v$ . But, in our ignorance of the relation between surface and body-density, all that we seek for from the above equation for  $l$ , is true values for  $l$  from measured values for  $\alpha$ . Accordingly the question arises, Can we choose temperatures at which to measure  $\alpha$  for different substances, so as to get true relative values of  $l$  irrespective of our ignorance of  $\bar{v}$ ?

As we have seen (Section 6) that at equal fractions of their critical temperatures, and under equal fractions of their critical pressures, one liquid is approximately a model of another on

a different scale, we conclude that if we use the value of the surface-tension measured at a constant fraction of the critical temperature, and under a constant fraction of the critical pressure, we ought to get correct relative values of  $l$ ; as surface-tension is not appreciably affected by pressure, we can dispense with the condition as to pressure and use measurements of  $\alpha$  made under a pressure of one atmosphere at a constant fraction of the critical temperature. I have chosen the fraction as two-thirds, because it gives a temperature near to the boiling-point of most liquids.

Schiff's abundant measurements (*Ann. der Chem.* cxxiii., and, further, *Wied. Beibl.* ix.) include not only the height to which different liquids rise in a capillary tube at their boiling-points, but also its temperature-coefficient, which is such as to show that the height in every case vanishes near the critical point.

Let  $H$  be the height to which a liquid rises in a tube of radius 1 millim.; then if  $H$  really vanished at the critical temperature and varied linearly with temperature, we should at  $2T_c/3$  have  $H = T_c b/3$ , where  $b$  is the temperature-coefficient. But to use this would be to depend too much on the accuracy of  $b$ .

If  $H_b$  is the value at  $T_b$  the boiling-point, then  $T_c = T_b + H_b/b$ , and

$$H = H_b + (T_b - 2T_c/3)b = H_b/3 + T_b b/3,$$

which depends partly on  $H_b$ , measured by Schiff, and partly on  $b$ . Now  $\alpha = H\rho/2 = H/2v$ ;

$$\therefore l \text{ or } c\alpha v^{2/3}/m^{1/3} = cHv^{2/3}/2m^{1/3},$$

$$l = c(H_b/3 + T_b b/3)v^{2/3}/2m^{1/3}.$$

If  $H$  is measured according to the usual practice as the height in millimetres for a tube of radius 1 millim., that is, if  $\alpha$  is measured in grammes weight per metre, then if  $l$  is desired in terms of the megadyne, gramme, and centimetre as units,  $c/2 = 5930$ , a mean value. Apart from all hypothesis about molecular force, our last relation between the virial constant and the constants of capillarity will be amply confirmed by the extensive comparisons soon to be presented in

Tables XXIV. and XXV. Meanwhile a few consequences of the relation may be glanced at.

9. *Establishment on Theoretical grounds of Eötvös's relation between surface-tension, volume, and temperature.*—According to the modified equation of the fourth method of finding  $l$ ,  $Ml=800T_c v_1$ ; and according to that of the fifth method,  $l=c\alpha v^{\frac{2}{3}}/m^{\frac{1}{3}}$ . The first of these equations would be more accurate if we replaced  $v_1$  by  $v$ , which in the second means the volume at  $2T_c/3$ ; so  $Ml=800T_c v$ , and  $m$  the actual mass of the molecule is proportional to  $M$  its molecular weight; so that from the second we have  $Ml$  proportional to  $\alpha(Mv)^{\frac{2}{3}}v$ , and hence  $\alpha(Mv)^{\frac{2}{3}}$  measured at  $2T_c/3$  is for all bodies proportional to  $T_c$ . Now in our notation the relation discovered by Eötvös (Wied. *Ann.* xxvii.) is

$$d\{\alpha(Mv)^{\frac{2}{3}}\}/dT=.227,$$

or

$$\alpha(Mv)^{\frac{2}{3}}=.227(T-T_c'),$$

where  $T_c'$  is a temperature very close to the critical; and this is only a more general statement of the relation we have just deduced.

As Eötvös has verified his relation experimentally for a large number of bodies, his result is a verification also of our general principles. The form of his relation also induces us to examine a little more closely an important consequence of the form of our infracritical equation, which, when multiplied by  $M$  with the  $pv$  term removed at low pressures, becomes

$$\frac{Ml}{2v}=R'M\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)T.$$

Now  $R'M$  is constant, and  $Ml/v$  is proportional to  $\alpha(Mv)^{\frac{2}{3}}$ , if  $\alpha$  and  $v$  are measured at  $2T_c/3$ , or any other constant fraction of the critical temperature, and under these circumstances  $\alpha(Mv)^{\frac{2}{3}}$  has been shown to be proportional to  $T_c$ ; hence if  $T$  is  $aT_c$ ,  $a$  being a constant fraction, we get  $T_c$  proportional to

$$\left(1+\frac{\sqrt{T}}{B}\cdot\frac{k'-v}{v-\beta}\right)aT_c,$$



so that  $1 + \frac{\sqrt{T}}{B} \cdot \frac{k' - v}{v - \beta}$ , measured at a constant fraction of the critical temperature, is approximately the same for all bodies, a result which our study of Van der Waals's generalization showed us to be approximately true. This shows that Eötvös's relation is rigorous only to the same extent as the constancy of this last expression is rigorous; as a matter of fact, excluding the alcohols and water, Eötvös finds the constant whose mean value is taken as .227 to depart from this mean value by not more than 5 per cent. in any individual case. This brief discussion of Eötvös's relation has therefore furnished us with additional proof of the general accuracy of the approximations we have been forced to make in parts of our work.

One of the main difficulties in the way of pushing on with the many interesting inquiries opened up by these relations lies in the fact that we do not know the relation between the densities in the body and in the surface-layer of a liquid.

We have to replace our relation

$$\alpha \text{ varies as } A\bar{\rho}^{\frac{5}{3}}m^{\frac{1}{3}}$$

by the less accurate one,

$$\alpha \text{ varies as } A\rho^{\frac{5}{3}}m^{\frac{1}{3}}.$$

Multiplying by  $(Mv)^{\frac{2}{3}}$  or  $(M/\rho)^{\frac{2}{3}}$ , we get the  $\alpha(Mv)^{\frac{2}{3}}$  of Eötvös proportional at all temperatures to  $AM\rho$ ; and as  $d\{\alpha(Mv)^{\frac{2}{3}}\}dT$  is constant, and has been shown by Eötvös to be constant almost right up to the critical temperature, and to be the same for all bodies, we ought, if our assumptions were rigorous, to have  $AMd\rho/dT$  constant almost up to the critical temperature and the same for all bodies (whence another approximate method of finding  $A$  or  $l$ ). Now  $d\rho/dT$  has been shown by Mendeléeff to be constant for many substances within ordinary temperature-ranges; but the constancy does not hold up to the critical temperature, and the ultimate meaning of the apparent contradiction between Eötvös's result and this is that, while for most purposes we may safely enough assume  $\bar{\rho}$  proportional to  $\rho$ , we cannot so accurately proceed to the consequence  $d\bar{\rho}^{\frac{5}{3}}/dT$  proportional to  $d\rho^{\frac{5}{3}}/dT$ ; in fact, a change

of temperature being accompanied by a change of stress in the surface-layer, the change of  $\bar{\rho}$  with temperature is more complex than that of  $\rho$ . But within the range of temperature for which  $d\rho/dT$  is approximately constant, we have the important result that

$$\frac{d}{dT} MR' \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} \right) T$$

is constant and is approximately the same for all bodies.

As I now consider the term differentiated to be not two thirds of the translatory kinetic energy of the gramme-molecule, but two thirds of the sum of the total kinetic energy and the chemic virial, I must replace the verbal statement of the last result as given in my paper (Phil. Mag. April 1889, p. 312) by the following :—The temperature-rate of variation of the sum of the total kinetic energy and the chemic virial of a molecule, measured at low constant pressure, is the same for all bodies (approximately).

10. *Tabulation of Values of the Virial Constant*, determined by four of the five methods described, and multiplied by the square of the molecular weight.—In the first place, I will give a comparison of the values of  $M^2l$  for those bodies to which existing data allow the application of three or four of the previously described methods. The multiplication by  $M^2$  is for future convenience. The values obtained by the second (liquid compression and expansion), third (latent heat), fourth (critical temperature), and fifth (capillarity) methods are entered in the columns marked 2, 3, 4, and 5. (The modified fourth method was used, namely,  $Ml=800T_c v_1$ .)

The units are the megamegadyne ( $10^{12}$  dynes), grm., and cm.

The satisfactory agreement of these values, calculated for such diverse bodies from such diverse data, must be taken as the verification of the main principles so far unfolded—the chief of which as regards molecular force is that for most compound bodies the internal virial term of the characteristic equation is  $l/2v$  below the volume  $k$ , and  $l/(v+k)$  above that volume.

TABLE XXIV.

Substance.	2.	3.	4.	5.
CS <sub>2</sub> .....	26.5	25.7	27.2	26.9
PCl <sub>3</sub> .....	.....	39.7	41.7	43.4
CCl <sub>4</sub> .....	.....	46.3	46.2	45.6
CHCl <sub>3</sub> .....	33.0	38.2	36.1	36.8
C <sub>2</sub> H <sub>5</sub> Cl .....	22.3	28.3	26.5	.....
C <sub>2</sub> H <sub>5</sub> Br .....	.....	32.1	31.5	29.0
C <sub>5</sub> H <sub>12</sub> .....	48.0	.....	45.3	47.1
C <sub>6</sub> H <sub>14</sub> .....	57.0	.....	58.5	59.3
C <sub>6</sub> H <sub>6</sub> .....	40.0	43.1	42.7	43.8
C <sub>7</sub> H <sub>8</sub> .....	59.0	55.8	56.2	56.4
(CH <sub>3</sub> ) <sub>2</sub> CO .....	.....	36.0	31.3	31.1
Methyl butyrate .....	65.0	60.4	55.6	56.1
Ethyl butyrate .....	84.0	74.6	69.5	71.3

We see, too, now how important for molecular dynamics is the detailed study of each of the constants  $k$ ,  $B$ , and  $\beta$  in the characteristic equations ; but for the present we must refrain from entering on such a study, and must consider the comparison in the last table as closing for the present the general discussion of the characteristic equation.

Our immediate object is now to ascertain the law connecting the value of  $M^2l$  for a body with its chemical composition. On the hypothesis of the inverse fourth power (with the subsidiary one of molecular swarms),

$$m^2l = \pi m^2 A (4 \log 2L/a - 16/3) ;$$

so that, the bracketed expression being the same for all bodies,  $m^2l$  is proportional to  $m^2A$ , and the law of  $m^2l$  or  $M^2l$  will be the law of  $m^2A$  in the expression  $3Am^2/r^4$  for the force between two molecules. In the Phil. Mag. for April 1889 I announced a law for the parameter  $A$ , calculated from Schiff's capillary data, which applied fairly well to a large number of organic compounds, but was affected with exceptions subversive of its generality. Applying now the more accurate method of calculation described as the fifth to all Schiff's data, we obtain ample material for generalization, which can be supplemented by values calculated by the other methods.

In the following Table the units are again the megamega-

dyne, grm., and cm. For brevity the radicals methyl, ethyl, and propyl, &c., will be denoted by the first two letters of their names, while the acid radicals—formic, propionic, &c.—will be denoted by Fot, Prt, and so on, so that PrPrt stands for propyl propionate. The numbers entered under the heading S will be explained when we are discussing the law of  $M^2$ .

TABLE XXV.—Values of  $M^2$ .

First Method.					
	$M^2$ .	S.		$M^2$ .	S.
Et <sub>2</sub> O .....	40.2	4.5	H <sub>2</sub> .....	.22	.04
CO <sub>2</sub> .....	7.1	1.07	N <sub>2</sub> .....	1.23	.205
SO <sub>2</sub> .....	15.0	2.05	O <sub>2</sub> .....	1.16	.195
NH <sub>3</sub> .....	8.5	1.25	CH <sub>4</sub> .....	2.2	.35
N <sub>2</sub> O .....	8.8	1.3	C <sub>2</sub> H <sub>4</sub> .....	6.5	1.0

Third Method.					
	$M^2$ .	S.		$M^2$ .	S.
SnCl <sub>4</sub> .....	61.3	6.1	IsoBuAct .....	76.2	7.1
AsCl <sub>3</sub> .....	49.0	5.2	EtBut .....	76.9	7.15
BCl <sub>3</sub> .....	23.5	2.95	PrPrt .....	77.3	7.2
SiCl <sub>4</sub> .....	47.3	5.05	IsoAmFot .....	78.7	7.3
CH <sub>3</sub> I .....	27.4	3.3	PrisoBut .....	89.1	8.0
EtI .....	40.0	4.5	EtVat .....	89.5	8.0
AmI(C <sub>5</sub> H <sub>11</sub> I) ..	88.3	7.9	IsoBuPrt .....	92.5	8.15
AmBr .....	61.8	6.15	IsoAmAct .....	93.1	8.15
AmCl .....	48.7	5.15	PrBut .....	92.5	8.15
C <sub>5</sub> H <sub>10</sub> .....	35.0	4.0	IsoBuisoBut .....	105	8.9
C <sub>10</sub> H <sub>20</sub> .....	90.4	8.0	PrVat .....	106	8.9
C <sub>10</sub> H <sub>16</sub> .....	109.0	9.1	IsoBuBut .....	109	9.1
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> .....	49.4	5.2	IsoAmPrt .....	110	9.15
Et <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .....	109.0	9.1	IsoAmisoBut .....	125	9.95
Et <sub>2</sub> O .....	44.1	4.8	IsoPrVat .....	126	10
EtFot .....	35.6	4.1	IsoAmBut .....	129	10.15
MeAct .....	36.0	4.1	IsoAmVat .....	147	11
EtAct .....	47.6	5.1	C <sub>8</sub> H <sub>8</sub> .....	43.1	4.7
MePrt .....	47.5	5.1	C <sub>7</sub> H <sub>8</sub> .....	55.8	5.7
PrFot .....	50.2	5.3	C <sub>6</sub> H <sub>5</sub> Et .....	69.5	6.65
MeButiso .....	60.4	6.04	C <sub>8</sub> H <sub>10</sub> (meta) .....	71.4	6.8
IsoBuFot .....	63.7	6.3	C <sub>8</sub> H <sub>5</sub> Pr .....	85.9	7.75
EtPrt .....	62.4	6.2	C <sub>8</sub> H <sub>12</sub> (mesitylene) ..	86.1	7.75
PrAct .....	62.8	6.2	C <sub>9</sub> H <sub>12</sub> (pseudo- cumene) .....	87.1	7.8
MeBut .....	61.8	6.15	C <sub>10</sub> H <sub>14</sub> (cymene) ..	101	8.6
EtisoBut .....	74.6	7.0			
MeVat .....	74.1	7.0			

Table XXV. (*continued*).

## Fourth Method.

	M%.	S.		M%.	S.
Cl <sub>2</sub> .....	5.8	.9	PrCl .....	34.6	4.0
H <sub>2</sub> S .....	10.5	1.5	NH <sub>3</sub> .....	10.0	1.4
C <sub>2</sub> H <sub>2</sub> .....	9.8	1.4	NH <sub>2</sub> Me .....	17.6	2.3
C <sub>3</sub> H <sub>6</sub> .....	14.7	2.0	NHMe <sub>2</sub> .....	23.5	3.0
C <sub>3</sub> H <sub>10</sub> .....	44.1	4.8	NMe <sub>3</sub> .....	31.6	3.7
CHCl <sub>3</sub> .....	36.9	4.2	NH <sub>2</sub> Et .....	21.2	2.7
CS <sub>2</sub> .....	27.0	3.3	NHEt <sub>2</sub> .....	41.4	4.55
C <sub>2</sub> N <sub>2</sub> .....	17.7	2.3	NEt <sub>3</sub> .....	65.5	6.4
HCl .....	7.9	1.15	NH <sub>2</sub> Pr .....	33.4	3.9
CH <sub>3</sub> Cl .....	15.6	2.1	NHPr <sub>2</sub> .....	67.6	6.5
EtCl .....	26.6	3.25			

## Fourth Method modified (not using critical pressures).

	M%.	S.		M%.	S.
(CH <sub>2</sub> Cl) <sub>2</sub> .....	38.0	4.3	EtC <sub>3</sub> H <sub>5</sub> O .....	48.6	5.15
CH <sub>3</sub> CHCl <sub>2</sub> .....	37.7	4.3	HCl .....	7.3	1.1
C <sub>6</sub> H <sub>5</sub> Cl .....	34.0	4.0	MeCl .....	16.8	2.2
CH <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub> .....	38.5	4.3	EtCl .....	26.4	3.2
(methylal) .....			PrCl .....	32.6	3.8
CH <sub>3</sub> CH(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> .....	68.7	6.6	NH <sub>3</sub> .....	7.6	1.1
(acetal) .....			NH <sub>2</sub> Me .....	15.6	2.1
C <sub>6</sub> H <sub>10</sub> .....	41.8	4.6	NHMe <sub>2</sub> .....	23.5	3.0
C <sub>6</sub> H <sub>10</sub> .....	51.2	5.4	NMe <sub>3</sub> .....	31.0	3.7
C <sub>8</sub> H <sub>18</sub> .....	80.5	7.4	NH <sub>2</sub> Et .....	24.4	3.05
C <sub>8</sub> H <sub>18</sub> .....	81.1	7.4	NHEt <sub>2</sub> .....	43.5	4.75
Me <sub>2</sub> O .....	20.3	2.6	NEt <sub>3</sub> .....	66.4	6.5
MeEtO .....	29.9	3.6	NH <sub>2</sub> Pr .....	31.0	3.7
EtPrO .....	52.4	5.45	NHPr <sub>2</sub> .....	68.6	6.6

## Fifth Method.

	M%.	S.		M%.	S.
EtFot .....	32.1	3.8	EtBut .....	72.3	6.85
MeAct .....	35.6	4.1	EtisoBut .....	71.3	6.8
PrFot .....	44.2	4.8	MeVat .....	69.7	6.7
EtAct .....	45.4	4.9	IsoAmAct .....	87.3	7.8
MePrt .....	44.8	4.85	IsoBuPrt .....	87.7	7.85
IsoBuFot .....	56.9	5.8	PrBut .....	89.3	7.95
PrAct .....	57.9	5.85	PrisoBut .....	87.7	7.85
EtPrt .....	58.5	5.9	EtisoVat .....	86.5	7.8
MeBut .....	58.2	5.9	IsoAmPrt .....	105	8.85
MeisoBut .....	56.1	5.75	IsoBuBut .....	106	8.9
IsoAmFot .....	71.6	6.8	IsoBuisoBut .....	103	8.75
IsoBuAct .....	70.6	6.75	PrisoVat .....	103	8.75
PrPrt .....	73.3	6.9			



Table XXV. (*continued*).

		M <sup>2</sup> l.	S.
C <sub>6</sub> H <sub>14</sub> .....	Normal hexane .....	59.3	6.0
C <sub>4</sub> H <sub>10</sub> .....	Diisobutyl .....	90.6	8.0
C <sub>10</sub> H <sub>22</sub> .....	Diisoamyl .....	125.6	10.0
C <sub>5</sub> H <sub>10</sub> .....	Amylene .....	45.0	4.9
C <sub>8</sub> H <sub>16</sub> .....	Caprylene .....	91.8	8.1
C <sub>10</sub> H <sub>16</sub> .....	Terpene .....	107.4	9.0
C <sub>6</sub> H <sub>10</sub> .....	Diallyl .....	54.8	5.6
C <sub>6</sub> H <sub>6</sub> .....	Benzene .....	43.8	4.75
C <sub>7</sub> H <sub>8</sub> .....	Toluene .....	56.4	5.75
C <sub>8</sub> H <sub>10</sub> .....	Orthoxylene .....	69.7	6.65
C <sub>8</sub> H <sub>10</sub> .....	Metaxylene .....	69.7	6.65
C <sub>8</sub> H <sub>10</sub> .....	Paraxyiene .....	70.3	6.7
C <sub>8</sub> H <sub>10</sub> .....	Ethylbenzene .....	70.6	6.7
C <sub>9</sub> H <sub>12</sub> .....	Normal propylbenzene .....	86.9	7.8
C <sub>9</sub> H <sub>12</sub> .....	Ethyltoluene .....	86.1	7.75
C <sub>9</sub> H <sub>12</sub> .....	Mesitylene .....	85.3	7.65
C <sub>10</sub> H <sub>14</sub> .....	Cymene .....	103.0	8.75
CHCl <sub>3</sub> .....	Chloroform.....	36.9	4.2
CCl <sub>4</sub> .....	Carbon tetrachloride .....	45.6	4.9
(CH <sub>2</sub> Cl) <sub>2</sub> .....	Ethylene chloride .....	44.4	4.8
CH <sub>2</sub> CHCl <sub>2</sub> .....	Ethidene chloride .....	38.1	4.3
PrCl .....	Propyl chloride .....	37.9	4.3
IsoBuCl.....	Isobutyl chloride .....	52.0	5.4
IsoAmCl .....	Isoamyl chloride .....	66.4	6.45
C <sub>6</sub> H <sub>5</sub> Cl .....	Chlorobenzene .....	57.7	5.85
C <sub>7</sub> H <sub>7</sub> Cl .....	Chlorotoluene .....	76.0	7.1
C <sub>7</sub> H <sub>7</sub> Cl .....	Benzyl chloride .....	82.2	7.5
C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub> .....	Propylene chloride.....	56.8	5.8
C <sub>2</sub> Cl <sub>4</sub> .....	.....	65.6	6.4
C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub> .....	Trichlorethane .....	58.2	5.9
C <sub>2</sub> H <sub>5</sub> ClO .....	Epichlorhydrin .....	49.8	5.25
CCl <sub>3</sub> COH .....	Chloral .....	50.9	5.35
CH <sub>3</sub> ClCO <sub>2</sub> Et.....	Ethyl chloracetate .....	63.2	6.25
CHCl <sub>2</sub> CO <sub>2</sub> Et.....	Ethyl dichloracetate .....	79.6	7.35
CCl <sub>3</sub> CO <sub>2</sub> Et .....	Ethyl trichloracetate .....	93.5	8.2
C <sub>6</sub> H <sub>5</sub> OCl .....	Benzoic chloride.....	79.6	7.35
C <sub>6</sub> H <sub>5</sub> Cl <sub>2</sub> .....	Benzilidene chloride .....	89.4	8.0
EtBr .....	Ethyl bromide .....	28.9	3.5
PrBr .....	Propyl bromide .....	41.4	4.6
IsoPrBr .....	Isopropyl bromide .....	41.2	4.6
C <sub>3</sub> H <sub>5</sub> Br .....	Allyl bromide.....	39.9	4.45
IsoBuBr .....	Isobutyl bromide .....	53.3	5.5
IsoAmBr .....	Isoamyl bromide .....	66.2	6.45
C <sub>6</sub> H <sub>5</sub> Br .....	Bromobenzene.....	66.8	6.5
C <sub>6</sub> H <sub>4</sub> Br .....	Orthobromotoluene .....	81.5	7.45
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> .....	Ethylene bromide .....	51.2	5.35
C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> .....	Propylene bromide .....	61.5	6.1
MeI .....	Methyl iodide .....	25.6	3.15
EtI .....	Ethyl iodide .....	38.1	4.3
PrI .....	Propyl iodide .....	50.9	5.3
IsoPrI .....	Isopropyl iodide.....	49.8	5.25
C <sub>3</sub> H <sub>7</sub> I.....	Allyl iodide.....	50.2	5.3
IsoBuI .....	Isobutyl iodide .....	62.4	6.2
IsoAmI .....	Isoamyl iodide .....	80.0	7.35

Table XXV. (*continued*).

		M <sup>2</sup> .	S.
$C_6H_5I$ .....	Iodobenzene .....	80.4	7.35
$NH_2Pr$ .....	Propyl amine .....	37.8	4.25
$NH_2C_3H_5$ .....	Allyl amine .....	36.6	4.2
$NH_2isoBu$ .....	Isobutyl amine .....	50.6	5.3
$NH_2isoAm$ .....	Isoamyl amine .....	64.4	6.3
$NHEt_2$ .....	Diethyl amine.....	50.1	5.5
$NEt_3$ .....	Triethyl amine .....	75.2	7.05
$NH_2C_6H_5$ .....	Aniline.....	65.0	6.35
$C_5H_5N$ .....	Pyridine .....	59.7	6.0
$C_5H_7N$ .....	Piperidine .....	100.3	8.6
$C_8H_7N$ .....	Chinoline.....	108.6	9.05
$MeNO_2$ .....	Nitromethane .....	22.6	2.75
$CCl_3NO_2$ .....	Chloropicrin .....	57.6	5.85
$EtNO_3$ .....	Ethyl nitrate .....	37.2	4.2
$isoAmNO_3$ .....	Isoamyl nitrate .....	76.9	7.2
$C_4H_7CN$ .....	Isobutylnitrile .....	39.2	4.4
$C_4H_9CN$ .....	Capronitrile .....	50.5	5.3
$C_6H_5CN$ .....	Benzonitrile .....	65.8	6.4
$CS_2$ .....	Carbon disulphide .....	26.9	3.3
$C_3N_2C_2H_5$ .....	Allyl sulphocarbimid .....	54.0	5.55
$CNSCH_3$ .....	Methyl sulphocyanate .....	33.7	3.9
$CNSC_2H_5$ .....	Ethyl sulphocyanate .....	44.1	4.8
$Et_2S$ .....	Ethyl sulphide .....	55.0	5.6
$PCl_3$ .....	.....	43.4	4.75
$POCl$ .....	.....	25.0	3.1
$POC_2H_5Cl$ .....	Ethoxyphosph. chloride .....	62.8	6.2
$PSCl$ .....	.....	35.5	4.1
$(CH_3)_2CO$ .....	Acetone .....	31.1	3.7
$C_6H_{12}O_3$ .....	Paraldehyde .....	85.7	7.7
$CH_3CH(OCH_3)_2$ .....	Dimethylacetal .....	53.3	5.5
$CH_3CH(OC_2H_5)_2$ .....	Diethylacetal .....	87.7	7.85
$Et_2O$ .....	Ethyl oxide .....	43.8	4.75
$(CH_3CO)_2O$ .....	Acetic anhydride .....	51.9	5.4
$CH_3CO_2C_2H_5$ .....	Allyl acetate .....	54.1	5.55
$MeisoAmO$ .....	Methylisoamyl oxide .....	66.8	6.5
$Et_2C_2O_4$ .....	Ethyl oxalate .....	91.0	8.05
$C_6H_5CO_2CH_3$ .....	Methyl benzoate .....	91.4	8.1
$C_6H_5CO_2C_2H_5$ .....	Ethyl benzoate .....	109.9	9.15
$CH_3(CO)_2CH_2OEt$ .....	Acetacetic ether .....	81.5	7.45
$C_6H_5OCH_3$ .....	Anisol .....	70.0	6.7
$C_6H_5OC_2H_5$ .....	Phenethol .....	80.7	7.4
$C_6H_5OCH_3$ .....	Methyl paracresolate.....	84.1	7.6
$C_6H_4(OCH_3)_2$ .....	Dimethyl resorcin .....	96.2	8.35
$C_4H_2OHCOH$ .....	Furfural .....	51.2	5.3
$C_4H_5COH$ .....	Valeraldehyde.....	48.0	5.1
$C_6H_{11}COH$ .....	Cuminol .....	113.0	9.3
$C_{10}H_{14}O$ .....	Carvol .....	117.8	9.6
$(CH_3)_3CCOCH_3$ .....	Pinakoline .....	63.5	6.3

The following are the chief sources of the data from which the above table has been constructed:—Latent Heats from Berthelot (*Chimie Mécanique*) and R. Schiff (*Ann. der Chem.* ccxxxiv.). Critical Temperatures from Sajontschewski (*Wied. Beibl.* iii.), Pawlewski (*Ber. deut. chem. Ges.* xv., xvi.), Nadejdine (*Wied. Beibl.* vii.), and Dewar (*Phil. Mag.* xviii.). Surface-tensions from R. Schiff (*Ann. der Chem.* ccxiii.; *Wied. Beibl.* ix.).

To make clear the two simple laws that rule these tabulated values, it will be advisable to confine our attention at first only to those values obtained by the fifth method, using those by other methods only to fill gaps. It will also be well to consider first a single chemical family, such as the paraffins, for which we have the following values :—

CH <sub>4</sub> .	C <sub>2</sub> H <sub>6</sub> .	C <sub>3</sub> H <sub>8</sub> .	C <sub>4</sub> H <sub>10</sub> .	C <sub>10</sub> H <sub>22</sub> .
2·2	14·7	59·3	90·6	125·6

These show that there is not a constant difference in the value of  $M^2l$  corresponding to the difference in the number of CH<sub>2</sub> groups contained. We can amplify this list of paraffins by using the material furnished by Bartoli and Stracciati (*Ann. de Chim. et de Phys.* sér. 6, t. vii.), who have determined the more important physical constants for all the paraffins from C<sub>5</sub>H<sub>12</sub> up to C<sub>16</sub>H<sub>34</sub>. Their values of the capillary constants were found at about 11 degrees in every case. To obtain those at two thirds of the critical temperature, we have to use the values of the critical temperatures calculated by them from Thorpe and Rücker's convenient empirical relation (*Journ. Chem. Soc.* xlv.),

$$\rho/(2T_c - T) = \text{constant},$$

$\rho$  being density at T.

The following are the values of  $M^2l$  thus obtained :—

C <sub>5</sub> H <sub>12</sub> .	C <sub>6</sub> H <sub>14</sub> .	C <sub>7</sub> H <sub>16</sub> .	C <sub>7</sub> H <sub>16</sub> .	C <sub>8</sub> H <sub>18</sub> .	C <sub>8</sub> H <sub>20</sub> .	C <sub>10</sub> H <sub>22</sub> .
47·2	58·1	77·1	79·6	91·2	110	127
C <sub>11</sub> H <sub>24</sub> .	C <sub>12</sub> H <sub>26</sub> .	C <sub>13</sub> H <sub>28</sub> .	C <sub>14</sub> H <sub>30</sub> .	C <sub>15</sub> H <sub>32</sub> .	C <sub>16</sub> H <sub>34</sub> .	
147	171	192	215	230	256	

Considering the assumptions involved in the calculation of these values and the difficulty of obtaining the paraffins pure, the agreement for C<sub>6</sub>H<sub>14</sub>, C<sub>8</sub>H<sub>18</sub>, and C<sub>10</sub>H<sub>22</sub> with Schiff's numbers is excellent; but the higher we go in the series the larger is the temperature-interval for which we have to extrapolate, and the more uncertain do the values become. However, they are useful as giving a general idea of the course of  $M^2l$  in an extended series.

On plotting these numbers as ordinates with abscissæ representing the number of CH<sub>2</sub> groups in the molecule, a curve was constructed which proved to be the parabola

$$M^2l = 6S + \cdot 66S^2,$$

where  $S$  is the number of  $\text{CH}_2$  groups. It is only necessary then to determine on this curve the abscissa corresponding to the value of  $M^2l$  for any substance to obtain the number of  $\text{CH}_2$  groups to which its molecule is equivalent as regards molecular force.

11. *Definition of the Dync Equivalent of a substance, and determination of its value for several Radicals.*—In the manner just described were obtained the numbers entered in Table XXV. under the heading  $S$ , which I propose to call the Dync Equivalents of the substances. The dync equivalent of a molecule is the number of  $\text{CH}_2$  groups in the molecule of the normal paraffin that exerts the same molecular force as it.

The table shows that the atom of an element contributes the same amount towards the dync equivalent of all molecules in which it occurs (except in the case of the simpler typical compounds): thus, for example, consider the iodides from methyl to amyl iodide, and notice that each  $\text{CH}_2$  group has the same value unity as in the paraffins, and that the iodine atom is equivalent to about  $2.3\text{CH}_2$  in every case. The same law holds throughout the table; so that each elementary atom or radical has its own dync equivalent, which can be easily determined.

In the first place, it appears that the extra  $\text{H}_2$  in the paraffins  $\text{C}_n\text{H}_{2n+2}$  can be neglected in a first approximation, because  $\text{C}_5\text{H}_{10}$  has practically the same dync equivalent as  $\text{C}_5\text{H}_{12}$ , and  $\text{C}_8\text{H}_{16}$  the same as  $\text{C}_8\text{H}_{18}$ . It may be that the double binding in the unsaturated compounds compensates for the  $\text{H}_2$  of the saturated, but I think that the simpler idea for the present is that the two terminal  $\text{H}$  atoms in a paraffin chain have a dync equivalent so small that we may neglect it, or more generally the middle  $\text{H}$  in a  $\text{CH}_3$  group is negligible in a first approximation. If there is really such a difference between the middle  $\text{H}$  and the two others in  $\text{CH}_3$ , we ought to find the dync equivalents for the iso-compounds smaller than for the normal; and the table shows that the isobutyrate have equivalents smaller by  $.1$  than the butyrate, while the isobutyl salts of the fatty acids have dync equivalents nearly all less than  $1$  greater than the propyl salts. But this is rather a matter for the chemist to work out in detail; it suffices to

indicate the idea here, and to point out that it is in harmony with the lowering of boiling-points among isomers with increasing number of  $\text{CH}_3$  groups. Accordingly, as a matter of detail, in the estimation of the dynic equivalents of the elements, it was assumed that the equivalent of  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n+1}$ , and  $\text{C}_n\text{H}_{2n}$  is in each case  $n$  when normal and  $n - 1\rho$  when the molecule departs from normality by  $p$   $\text{CH}_3$  groups. (In constructing my curve for dynic equivalents, for the sake of simplicity at first, I ignored the fact that two of the paraffins in Schiff's data are iso-compounds.)

From the tabulated values for the alkyl salts of the fatty acids, we get the following mean values for the dynic equivalent of  $\text{CO}''\text{O}'$ :—in the formiates 1.85, acetates 1.92, propionates 1.91, butyrates 1.92, isobutyrate 1.91, and isovalerates 1.83, the mean for all being 1.9.

From the oxides (ethers) and other compounds containing single-bound O, we find for its mean value .6, although in the ethers containing the benzene nucleus it comes out .8, while in the benzoates  $\text{CO}''\text{O}'$  is about 2.5; so that the junction of the benzene nucleus with other groups seems to be accompanied with an increase in its value: witness also the bromide, iodide, and amine of  $\text{C}_6\text{H}_5$ , equal to the bromide, iodide, and amine of  $\text{C}_5\text{H}_{11}$ , although  $\text{C}_6\text{H}_6$  is less than  $\text{C}_5\text{H}_{12}$  by .25. This slight variation of the value of  $\text{C}_6\text{H}_6$  is the only anomaly amongst the numbers of Table XXV. excepting the simple typical compounds. The values .6 for  $\text{O}'$  and 1.9 for  $\text{C}''\text{O}'$  are in harmony with the results for all the other compounds containing oxygen.

From the values for the benzene series of hydrocarbons we can get a value for  $\text{H}_2$  in  $\text{CH}_2$ , and also some light on the important question of the structure of the benzene nucleus. Thomsen has been led by his thermochemical investigations to the conclusion that in benzene each carbon atom is bound to three other carbon atoms by a single bond to each (the "bond" phraseology is used merely for brevity, and not as expressing definite statical or dynamical facts). If we accept this conclusion, then the dynic equivalent of  $\text{C}_6\text{H}_{12}$  minus that for  $\text{C}_6\text{H}_6$  is equal to the dynic equivalent of  $3\text{H}_2$ ; similarly, from the other members of the benzene series we get the values for  $3\text{H}_2$ , the mean result being 1.29 or .43 for  $\text{H}_2$ .

The accepted structure for  $\text{C}_6\text{H}_{10}$  diallyl is  $(\text{CH}_2\text{CHCH}_2)_2$ , or four whole  $\text{CH}_2$  groups and two  $\text{CH}_2$  groups with H removed



from each; and as the dynic equivalent of  $C_6H_{10}$  is 5·6, we find that of  $H_2$  to be ·4. Again, recent investigations on the terpenes (Wallach, *Ann. der Chem.* ccxxv., ccxxvii., ccxxx.; Brühl, ccxxxv.) show that the two ordinary forms can have their formulæ written  $CH_3C_3H_7(CH_2)_2(CH)_2C_2$ ; that is to say, they have 6 hydrogen atoms cut out of  $CH_2$  groups, and as the dynic equivalent of  $C_{10}H_{16}$  is 9 we have that of  $3H_2$  as 1·0 or that of  $H_2$  ·33. Since the value ·43 is derived from 10 accordant members of the benzene series, we will take it as the value of the dynic equivalent of  $H_2$  in  $CH_2$ .

By similar but simpler reasoning the dynic equivalents of Cl, Br, I, and other radicals are easily found, and the following is a list of mean values:—

TABLE XXVI.—Dynic Equivalents.

$CH_2$ .	H.	C.	$C''O'$ .	$O'$ .	$NH_2$ .	CN.
1·0	·215	·57	1·9	·6	1·23	1·35
$NO_3$ .	CNS.	$S'$ .	Cl.	Br.	I.	
2·2	2·85	1·6	1·3	1·6	2·3	

To illustrate the applicability of these values, I furnish a comparison of the values calculated by means of them for twenty substances with the values tabulated in Table XXV.

TABLE XXVII.

Comparison of calculated and tabulated Dynic Equivalents.

	Calc.	Tab.		Calc.	Tab.
$C_6H_8$ .....	4·8	4·75	$C_4H_5CN$ .....	5·35	5·3
$C_{10}H_{14}$ .....	8·8	8·75	$C_4H_{10}S$ .....	5·6	5·6
$C_3H_7Cl$ .....	4·3	4·3	$C_5H_5CNS$ .....	4·85	4·8
$C_5H_{11}Cl$ .....	6·3	6·45	$(CH_3)_2O$ .....	2·6	2·6
$C_5H_5Br$ .....	3·6	3·5	$CH_3C_5H_{11}O$ .....	6·6	6·5
$C_5H_{11}Br$ .....	6·6	6·45	$C_6H_{12}O_3$ .....	7·8	7·7
$C_2H_5I$ .....	4·3	4·3	$(CH_3CO)_2O$ .....	5·2	5·4
$C_5H_{11}I$ .....	7·3	7·35	$C_4H_5COH$ .....	5·3	5·1
$NH_2C_3H_7$ .....	4·23	4·25	$C_4H_5O_2$ .....	4·9	4·9
$NH_2C_5H_{11}$ .....	6·23	6·3	$C_7H_{14}O_2$ .....	7·9	7·9

If we now look at the dynic equivalents of the uncombined elements given in the first part of Table XXV., we may notice that they are remarkably small compared to the values in the combined state; thus, that of  $H_2$  is  $\cdot 04$ , of  $N_2$   $\cdot 205$ , of  $O_2$   $\cdot 195$ , and that of  $CH_4$  is small too,  $\cdot 35$ , instead of 1 as it should be, seeing that  $CH_4$  is the first of the paraffin series. Other typical compounds have small values:  $CO_2$  has  $1\cdot 05$ , while  $CO''O'$  in more elaborate compounds has a value  $1\cdot 9$ ,  $C_2H_4$  has 1, while  $C_2H_6$  has 2; and so on. The same fact has been noticed in connexion with the molecular refraction of some of the typical compounds and some of their immediate derivatives, and it will yet prove a most important one in chemical dynamics. But meanwhile it is of greater importance for present purposes to notice that the dynic equivalents given for various radicals in Table XXVI. are closely proportional to their molecular refractions.

12. *Close parallelism between Dynic Equivalents and Molecular Refractions.*—As is well known, there are two methods according to which the molecular refraction is estimated, the first by means of Gladstone's expression,  $(n-1)M/\rho$ , where  $n$  is index of refraction; the other by means of Lorenz's,  $(n^2-1)M/(n^2+2)\rho$ .

In a brief paper (Phil. Mag. Feb. 1889) I showed that the experimental evidence taken as a whole is in favour of the Gladstone expression, for which also a very simple theoretical proof can be given; and, further, it was shown that it is best to measure  $(n-1)M/\rho$  if possible in the gaseous state. But as comparatively few measurements have been made on bodies in the vapour state I suggested that, as the Lorenz expression had been empirically proved to give more nearly the same value in the liquid and vapour states of a body, its value as determined in the liquid state and multiplied by  $3/2$  could be taken as giving the value of  $(n-1)M/\rho$  in the vapour state. The result of the theoretical argument was that, if  $M/\rho$  is taken to measure the molecular domain  $u$ , and if  $U$  is the volume occupied by the molecule in the same units, and  $N$  is the index of refraction for the matter of the molecule, then

$$(n-1)u = (N-1)U.$$

Landolt, Brühl, and others have determined the values of the atomic refraction for several elements (*Ann. der Chem.* ccxiii. p. 235), and by means of these and Masini's data for sulphur (*Wied. Beibl.* vii.) and Gladstone's latest determinations (*Journ. Chem. Soc.* 1884), I have obtained the values of the refraction-equivalents of the preceding radicals in terms of that for  $\text{CH}_2$  as unity. Mascart has given (*Compt. Rend.* lxxxvi.) values of the refraction of a number of substances in the vapour state, from which, for the sake of comparison, I have calculated the refraction-equivalents for as many radicals as possible.

The following Table contains in the second column the dynic equivalent, in the third the refraction-equivalent calculated according to the Lorenz expression, in the fourth the refraction-equivalent calculated according to the Gladstone expression from Mascart's data for vapours, and in the fifth that calculated by Gladstone from liquid data. The value for  $\text{CH}_2$  in every case is 1.

TABLE XXVIII.

Comparison of Dynic and Refraction Equivalents.

1.	2.	3.	4.	5.
$\text{CH}_2$ .....	1.0	1.0	1.0	1.0
H .....	.215	.23	.19	.17
C .....	.57	.54	.62	.66
$\text{CO}''\text{O}'$ .....	1.9	1.4	1.5	1.5
$\text{O}'$ .....	.6	.35	.4	.37
$\text{NH}_2$ .....	1.23	1.12	.....	1.01
$\text{CN}$ .....	1.35	1.18	1.3	1.2
$\text{NO}_3$ .....	2.2	2.2	.....	1.9
$\text{CNS}$ .....	2.85	.....	.....	3.0
$\text{S}'$ .....	1.6	1.7	.....	1.9
Cl .....	1.3	1.3	1.5	1.3
Br .....	1.6	2.0	1.7	2.0
I .....	2.3	3.1	2.7	3.2

This table brings out the remarkable fact that the parallelism between the dynic and refraction-equivalents is so close as almost to amount to proportionality. I shall not discuss the meaning of this relation until I have shown how to obtain the dynic equivalents for the elements usually

occurring in inorganic compounds, and established the same relation for them also.

Meanwhile it will be useful to compare the dynic and refraction equivalents of the uncombined elements and of those simpler typical compounds to which we have said the summative law does not apply as regards dynic equivalents and does not accurately apply as regards refraction-equivalents.

TABLE XXIX.

Ratio of Dynic to Refraction Equivalents, each measured  
in terms of that for  $\text{CH}_2$  as unity.

$\text{H}_2$ .	$\text{O}_2$ .	$\text{N}_2$ .	$\text{Cl}_2$ .	$\text{CH}_4$ .	$\text{C}_2\text{H}_4$ .	$\text{H}_2\text{S}$ .	$\text{C}_2\text{H}_2$ .	$\text{CHCl}_3$ .	$\text{CS}_2$ .
·09	·21	·22	·38	·32	·45	·79	·75	·94	·72
$\text{C}_2\text{N}_2$ .	$\text{HCl}$ .	$\text{CH}_3\text{Cl}$ .	$\text{NH}_3$ .	$\text{CO}_2$ .	$\text{SO}_2$ .	$\text{N}_2\text{O}$ .	$\text{PCl}_3$ .	$\text{CCl}_4$ .	$(\text{CH}_3)_2\text{O}$ .
·90	·83	·79	1·06	·76	·96	·83	·88	·89	·86

We see that the ratio is small for the uncombined elements and  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$ , a result of the important fact that while the refraction-equivalent of a non-metallic element is almost the same in the uncombined state as in the combined, the dynic equivalent is much smaller in the uncombined state of an element. The meaning of this fact will be discussed later on ; connected with it is the fact that the ratio for most of the typical compounds in the last table is notably less than unity. A molecule has to reach a certain degree of complexity before the summative law holds as regards its dynic equivalent ; the same may be said about its heat of formation. Further comment on the connexion between dynic equivalent and heat of formation must be deferred for a little.

We can now give a formal enunciation of the law of the virial constant :—If the molecule of an organic compound is of a degree of complexity higher than that of the ordinary typical compounds, then the virial constant for one gramme

of the compound is given in terms of the megamegadyne, gramme, and centimetre as units by the relation

$$M^2l = 6S + \cdot66 S^2,$$

where  $M$  is the usual molecular weight of the compound, and  $S$  is the sum of the dynic equivalents of the atoms in its molecule (measured in terms of that for  $\text{CH}_2$  as unity).

According to the law of force  $3Am^2/r^4$ ,  $Am^2$  is proportional to  $M^2l$  and therefore follows the same law.

13. *Return to the Discontinuity during Liquefaction of Compounds and proof that it is due to the pairing of Molecules.*

—The interpretation of the form of the internal virial expression above the volume  $k$  is of the highest importance in the theory of molecular force, and can now be attempted in the light of the law for  $M^2l$ . If the molecules of a substance do pair to produce an actual chemical polymer of it, then its molecular mass changes from  $M$  to  $2M$ , while  $S$  the dynic equivalent changes to  $2S$ , and consequently

$$l \text{ or } (6S + \cdot66 S^2)/M^2$$

changes to a value given by

$$l' = (6S/2 + \cdot66 S^2)/M^2.$$

When  $S$  is small we see that the pairing of molecules to produce a polymer causes the virial constant (for one gramme) to diminish to nearly the half of its value for free molecules; when  $S$  is larger this statement becomes less exact. In the case of  $\text{CO}_2$ , for example, if from Table XXV. we take  $S$  as 1.05, then

$$l = \cdot00367 \quad \text{and} \quad l' = \cdot00206,$$

but in the case of ethyl oxide, with  $S = 4.5$ ,

$$l = \cdot00738 \quad \text{and} \quad l' = \cdot00491.$$

In both cases we see that the pairing of the molecules to form a new chemical compound or polymer is attended with a reduction of the virial constant towards one half, but not exactly to one half of the original value. Now the data given in Tables I. and III. and the form of virial term taken to represent them,  $l/(v+k)$ , along with the fact that



below volume  $k$  the form is  $l/2v$ , mean that in the limiting gaseous state the virial term is practically  $l/v$ , just as below  $k$  it is  $l/2v$ ; hence we must regard the pairing of the molecules to be such as to cause the virial constant to become one half of its higher limit—in other words, the pairing must be different from polymerization. We are therefore led to differentiate the chemical and physical pairing of molecules by the statement that while chemical pairing alters the virial constant in the ratio

$$(6S + \cdot66S^2)/(12S + 2\cdot64S^2) \text{ or } (1 + \cdot11S)/(2 + \cdot44S),$$

physical pairing alters it in the ratio

$$6S/12S \text{ or } 1/2.$$

The term  $\cdot66S^2$  would thus appear to have a certain chemical significance.

And now as to the form  $l/(v+k)$  connecting the two extreme cases. We can explain it in the following manner:—It will be shown when we come to treat of solutions that if a salt having a parameter of molecular force  $3A$  (proportional to its virial constant  $l$ ) is dissolved in a solvent with parameter  $3W$  so that there are  $n$  molecules of salt to one of solvent, then the solution behaves as if it consisted of molecules having a parameter  $3X$  given by the singular relation

$$X^{-1} = (W^{-1} + nA^{-1})/(1+n).$$

Now, in a gas being compressed towards the volume  $k$ , let us assume that there are a number of pairs of molecules proportional to  $k$  and a number of single molecules proportional to  $v-k$ , and that the same relation applies to the mixture of paired and single molecules as to the solvent and salt in a solution, then, replacing  $W$  by  $l$  and  $A$  by  $l/2$  and  $n$  by  $k/(v-k)$ , we get for the reciprocal of the virial constant of the mixture

$$X^{-1} = \left( \frac{1}{l} + \frac{k}{v-k} \cdot \frac{2}{l} \right) / \left( 1 + \frac{k}{v-k} \right) = \frac{1}{l} \cdot \frac{v+k}{v};$$

$$\therefore X = lv/(v+k),$$

and therefore the virial term is  $l/(v+k)$ .

This would be no demonstration of the pairing of molecules in compounds, if we did not already have it proved in the case of the elements that the virial term varies inversely as the volume at all volumes. Remembering this we can accept our form  $l/(v+k)$  as indicating the existence of a mixture of paired and single molecules, the number of pairs at volume  $v$  being to the number of single molecules as  $k$  to  $v-k$ .

The form of the energy term,

$$RT \left( 1 + \frac{2k}{v+k} \right),$$

must also be partly determined by this existence of pairs, but it would be foreign to our immediate subject to attempt to investigate it.

14. *Brief Discussion of the Constitution of the Alcohols as Liquids.*—To learn a little more on the subject of pairing, it will be of some profit to consider briefly here the alcohols and water, which so far have been left aside, after having been proved in Table XII. to follow in the supracritical region a different law from the usual one. But also in the liquid state the alcohols and water, while conforming to the general liquid laws in many respects, are still exceptional in others. Thus Eötvös (Wied. Ann. xxvii.) has shown that the alcohols will conform to his generalization if at the lower range of temperature, from 20° C. to 170° C., the molecules be considered complex (double relatively to ordinary liquids), and water also conforms if from 100° upwards its molecules be considered double; the molecular lowering of the freezing-point of water produced by the solution of bodies in it as measured by Raoult and compared with the molecular lowering for other liquids proves that relatively to these the molecule of water is double. Taking all the facts into consideration, it seems to me that the alcohols and water may be assumed, in the liquid state, to have the pairs of molecules again paired, the second pairing, however, not being of so intimate a nature as the first, consisting of a mere approximation of the first pairs without any change in the values of  $A$  or of  $l$ .

According to this assumption we should expect the beha-

viour of the liquid alcohols to be represented by a form similar to our infracritical equation, and we will assume

$$pv = R''T \left( 1 + \frac{\sqrt{T}}{B} \cdot \frac{k'-v}{v-\beta} \right) - \frac{l}{2v},$$

where  $R''$  is about  $2R$ .

It was on the infracritical equation that our second method of finding  $M^2l$  was founded, giving the relation

$$l = \frac{4}{3} \left( v_0 \frac{a}{\mu} + \frac{25}{26} R \right) vT,$$

which can be applied to Amagat's data (*Ann. de Chim. et de Phys.* sér. 5, t. xi.), and Pagliani and Palazzo's (*Wied. Beibl.* ix.) for the alcohols.

Again, our assumption enables us to apply the fifth or capillarity method of finding  $M^2l$  to the alcohols, if only we remember that the molecular domain becomes twice as large and its radius  $2^{\frac{1}{2}}$  as large as it would be with only one pairing; hence the equation for the fifth method becomes for the alcohols

$$l = c \alpha v^{\frac{1}{2}} / (2m)^{\frac{1}{2}}.$$

Schiff's data are available.

As the latent heat and critical temperature are largely dependent on the supracritical equation, we ought not to expect the formulæ for  $M^2l$  furnished by the third or latent-heat method and by the fourth or critical-temperature method to apply to the alcohols. But as the relation

$$M\lambda = 19.4T_b,$$

or, empirically,

$$M\lambda = 21 T_b,$$

which was deduced in the discussion of the third method, does apply approximately to the alcohols, the constant being 26, we may as well, for purposes of comparison, see what the formulæ of the third and fourth methods give in the case of the alcohols.

TABLE XXX.— $M^2l$  for the Alcohols.

Method .....	Second.	Third.	Fourth.	Fifth.
Methyl .....	8	22 (11)	17 (9)	9.4
Ethyl.....	14	38 (19)	25 (17)	17.6
Propyl .....	24	.....	34 (26)	27.8
Isopropyl .....	24	.....	33 (25)	27.6
Isobutyl.....	34	.....	46 (38)	37.8
Isoamyl.....	47	82 (41)	57 (49)	48.1
Cetyl.....	.....	326 (163)	.....	.....
Water .....	.....	11 (5.5)	9	6

The second and fifth methods give results in substantial agreement with one another; the third gives numbers which, when halved as in the brackets, come into agreement with the others; while if 8 be subtracted from the numbers furnished by the fourth method as in the brackets, the resulting numbers are in very close agreement with those given by the fifth method. That the two discrepant columns should be capable of harmonization with the two others by the simple operations of halving and of subtracting a constant is significant of some really simple principle on which the abnormality of the alcohols in the supracritical region depends.

But too much importance must not be attached to the general agreement among the numbers, as they are all founded on tentative assumptions; they simply prove that our idea of a second loose pairing of molecular pairs in the liquid alcohols is not discordant with facts.

The following are the dynic equivalents corresponding to the values of  $M^2l$  found by the fifth method compared with those calculated from the dynic equivalents of the elements and placed in the third row.

Alcohols .....	Methyl.	Ethyl.	Propyl.	Butyl(iso).	Amyl(iso).
Dynic equiv. found	1.35	2.35	3.4	4.3	5.1
„ „ calcul.	1.8	2.8	3.8	4.7	5.7

For water the dynic equivalent found is .91, while 1.03 is the calculated value. The values found for the alcohols are about .5 smaller than those calculated. If from the capillarity data we had calculated the values of  $M^2l$  and the dynic

equivalent as if the alcohols were not exceptional in any way, we should have got:—

Alcohols .....	Methyl.	Ethyl.	Propyl.	Butyl.	Amyl.
M <sup>2</sup> l. . . . .	11·8	22·2	35	47·6	60·6
Dynic equivalent	1·65	2·8	3·9	5·1	6·1

These values of the dynic equivalents agree well with the calculated ones above, but then the values of M<sup>2</sup>l being all increased in the ratio of 2<sup>2/3</sup> to 1 are no longer in agreement with the values got by the second method.

Accordingly we see that the alcohols will require an exhaustive study for themselves, if the interesting features of their molecular structure are to be thoroughly made out. I have merely sketched lines on which their abnormality may be hopefully investigated. Those bodies, such as nitric peroxide, studied by the brothers Natanson, and acetic acid, studied by Ramsay and Young, which have been proved to have double molecules split up both by the action of heat and reduction of pressure have not been touched on in this paper; they also would require a special investigation in which our characteristic equations would lend an assistance much required.

15. *Methods of finding the Virial Constant for Inorganic Compounds, including a Theory of the Capillarity and Compressibility of Solutions.*—So far I have secured only two methods of finding the virial constants and dynic equivalents of inorganic compounds from existing data, and only one of these is practically useful, namely the first, in which the surface-tensions of solutions are the source of the values; the second is based on the compressibility of solutions. Using our expression for surface-tension in terms of molecular force,

$$\alpha = \pi \bar{\rho}^2 A e / (2 + \sqrt{2}),$$

in the form

$$\alpha = A \rho^{\frac{2}{3}} m^{\frac{1}{3}} / c,$$

where  $c$  is a constant, I was led to imagine that it could be adapted to the case of a solution by means of the following suppositions:—First, that in a solution containing  $n$  molecules of dissolved substance of molecular mass  $p$  to one of



solvent of molecular mass  $w$ , the solution may be assumed to be a substance of molecular mass

$$m = (w + np)/(1 + n);$$

second, that if  $3W$  is the parameter of molecular force for the solvent and  $3A$  for the dissolved substance, then the parameter  $3X$  for the solution is connected with  $W$  and  $A$  by the relation

$$X^{-1} = (W^{-1} + nA^{-1})/(1 + n).$$

This seems highly arbitrary, but will be completely verified by the results to which it leads. I could make no progress in the handling of solutions until, in the course of some work on the elasticity of alloys, I discovered a relation similar to the above to hold, and this proved to be the immediate clue to the treatment of solutions.

Let  $\alpha_w$  be the surface-tension of water, then we have the following equations giving  $A$  :—

$$a = X\rho^{\frac{1}{3}} \left( \frac{w + np}{1 + n} \right)^{\frac{1}{3}} / c, \quad \alpha_w = Ww^{\frac{1}{3}}/c,$$

$$A^{-1} = X^{-1} + (X^{-1} - W^{-1})/n.$$

These equations ought to give the same values of  $A^{-1}$  whatever the strength of the solution may be; and herein lies a first test of the truth of the principles involved.

The following values of  $cA^{-1}$  for NaCl are calculated from Volkmann's data (*Wied. Ann.* xvii.) for its solution in water at  $20^\circ$ ;  $w$  is taken as 18, although we consider the water molecule to be complex, but this does not affect the purely relative comparison being made :—

$n$	. . .	·105	·084	·052	·035	·017
$cA^{-1}$	. .	1·34	1·38	1·47	1·46	1·42

Considering that the solutions range from saturation down to considerable dilution, the approach to constancy is satisfactory; but it will be noticed that, on the whole, there is a tendency for the value of  $cA^{-1}$  to increase with diminishing concentration, and this same phenomenon is to be seen in the case of almost all Volkmann's solutions, most pronouncedly in that of  $\text{CaCl}_2$  :—

$n$	. . .	·091	·068	·041	·021	·011
$cA^{-1}$	. .	2·41	2·53	2·77	2·95	3·12

This case shows us that there is a certain amount of incompleteness in our theory of the capillarity of solutions, as indeed we ought to be surprised if there were not, when we try to apply our arbitrary definition of the molecular mass of a solution to one which contains 56 parts by weight of  $\text{CaCl}_2$  to 100 of  $\text{H}_2\text{O}$  as the solution for which  $n = \cdot 091$  does, and also when we assume that the concentration in the surface-layer is the same as in the body-fluid at all strengths up to saturation. If our object were an exhaustive representation of the connexion between the surface-tension of a solution and its concentration, it would be easy to introduce a slight empirical alteration into the above equations to make them exhaustive. For instance, we might imagine that the effective value of  $W$  in a solution experiences a small change proportional to the concentration; but the equations as they stand will prove to be sufficient for our purpose if, in comparing solutions of different substances, we calculate  $cA^{-1}$  for the same value of  $n$  throughout.

In all subsequent calculations  $n = 18/1000$ . The experimental data for surface-tensions of solutions are abundant, the chief that I know of and have used being those of Valson (*Compt. Rend.* lxx., lxxiv.), Volkmann (*Wied. Ann.* xvii.), Röntgen and Schneider (*Wied. Ann.* xxix.), and Traube (*Journ. für Chem.* cxxxix.).

The following Table contains the values of  $cA^{-1}$  for a certain number of compounds, the surface-tension being measured in grammes weight per linear metre and the half molecules of the salts of the bibasic acids being regarded as molecules.

TABLE XXXI.—Values of  $cA^{-1}$ .

	I.	Br.	Cl.	$\text{NO}_3$ .	OH.	$\frac{1}{2}\text{SO}_4$ .	$\frac{1}{2}\text{CO}_3$ .
Li .....	4.15	2.46	.83	1.61	.83	1.61	
$\text{NH}_4$ .....	3.99	2.21	.70	1.54	...	1.45	
Na .....	4.74	3.06	1.45	2.30	1.37	2.30	1.95
K .....	4.99	3.31	1.78	2.55	1.71	2.72	2.21

The study of this table brings out the fact that the differences of the numbers in any two rows or in any two columns are constant: thus the differences for the iodide and chloride of the four bases are in order 3.32, 3.29, 3.29, and 3.21, while the differences of  $cA^{-1}$  for the Na and Li salts of the monobasic acids are in order .59, .60, .62, .69, and .54. Accordingly

each atom contributes a certain definite part to the value of  $cA^{-1}$  for the molecule in which it occurs, and that part is independent of the other atoms in the molecule. I shall call this part the parameter-reciprocal modulus of the atom; we have not at present sufficient data to get its absolute value in any case, but if we make Li our standard positive radical, and Cl the standard negative, we can calculate the average values of the difference between the parameter-reciprocal modulus of a radical and its standard,—thus in the case of iodine this difference is 3·28, and in the case of Na ·61, and so on.

Before tabulating these mean values I will give the values calculated for the salts of some other metals with the values for the same salts of Li subtracted.

TABLE XXXII.

	I.	Br.	Cl.	NO <sub>3</sub> .	$\frac{1}{2}$ SO <sub>4</sub> .
$\frac{1}{2}$ Mg—Li.....	...	...	·39	·35	·53
$\frac{1}{2}$ Ca —Li.....	·44	·73	·67	·55	...
$\frac{1}{2}$ Sr —Li.....	...	...	1·67	1·71	...
$\frac{1}{2}$ Ba —Li.....	...	...	2·49	2·52	...
$\frac{1}{2}$ Zn —Li.....	...	...	1·35	...	1·33
$\frac{1}{2}$ Cd —Li.....	2·24	2·42	2·15	...	2·29
$\frac{1}{2}$ Mn—Li.....	...	...	1·17	·93	1·22

To these we may add the following values, obtained from the sulphates  $\frac{1}{2}$ Fe—Li 1·27,  $\frac{1}{2}$ Ni—Li 1·19,  $\frac{1}{2}$ Co—Li 1·15,  $\frac{1}{2}$ Cu—Li 1·49,  $\frac{1}{3}$ Al—Li ·6,  $\frac{1}{3}$ Fe<sub>ic</sub>—Li ·5, and  $\frac{1}{3}$ Cr<sub>ic</sub>—Li 1·0; and the two following from the nitrates Ag—Li 3·91, and  $\frac{1}{2}$ Pb—Li 4·51.

The following Table contains the values of the parameter-reciprocal moduluses of the different metals minus that for Li and of the negative radicals minus that for Cl.

TABLE XXXIII.

Mean Values of Parameter-reciprocal Modulus for the Metals with that for Li subtracted.

Na.	K.	NH.	$\frac{1}{2}$ Mg.	$\frac{1}{2}$ Ca.	$\frac{1}{2}$ Sr.	$\frac{1}{2}$ Ba.	$\frac{1}{2}$ Zn.	$\frac{1}{2}$ Cd.	$\frac{1}{2}$ Mn.
·61	·90	—·15	·42	·65	1·7	2·5	1·33	2·3	1·2
$\frac{1}{2}$ Fe <sub>ous</sub> .	$\frac{1}{2}$ Ni.	$\frac{1}{2}$ Co.	$\frac{1}{2}$ Cu.	Ag.	$\frac{1}{2}$ Pb.	$\frac{1}{3}$ Al.	$\frac{1}{3}$ Fe <sub>ic</sub> .	$\frac{1}{3}$ Cr <sub>ic</sub> .	
1·27	1·2	1·15	1·5	3·9	4·5	·6	·5	1·0	

The same for negative radicals with that for Cl subtracted:—

I.	Br.	NO <sub>3</sub> .	OH.	$\frac{1}{2}$ SO <sub>4</sub> .	$\frac{1}{2}$ CO <sub>3</sub> .
3.28	1.56	.81	.04	.86	.46

It may be worth mentioning that these differences show a pretty close parallelism to the corresponding differences of the atomic refraction given by Gladstone (Phil. Trans. 1870), but not close enough to be worth dwelling on.

In the case of the organic bodies studied there was nothing analogous to this singular property possessed by these inorganic compounds of having the reciprocal of the parameter  $A$  of molecular force separable into a constant and definite parts contributed by each constituent of the molecule. Thus we have characteristic of inorganic bodies in solution another of those properties called by Valson modular, who discovered that the density, capillary elevation, and refraction of normal solutions (gramme-equivalent dissolved in a litre of water) could all be obtained from the values for a standard solution such as that of LiCl by the addition of certain numbers or moduluses representing invariable differences for the metals and Li and for the negative radicals and Cl. Other properties of solutions have since been proved to be modular, as for instance their heats of formation from their elements and their electric conductivities. I think the modular nature of some of these properties of solutions is the outcome of this modular property in the parameter reciprocal of molecular force along with the additive property in mass. To prove this in the case of density would require a special investigation, but if we assume the property for density we can easily deduce Valson's result that the property applies to capillary elevation. Let  $h$  be the height to which a normal solution of any salt RQ rises in a tube of radius 1 millim., then

$$h = 2\alpha/\rho = 2X\rho^{\frac{2}{3}}\left(\frac{w + np}{1 + n}\right)^{\frac{1}{3}}/c.$$

Let  $r$  and  $q$  be the density moduluses of the radicals R and Q, being small fractions, then  $\rho = d + r + q$ , where  $d$  is a constant nearly 1; also

$$X^{-1} = (W^{-1} + nA^{-1})/(1 + n),$$

so that

$$h = 2\left(\frac{1 + n}{W^{-1} + nA^{-1}}\right)(d + r + q)^{\frac{2}{3}}\left(\frac{w + np}{1 + n}\right)^{\frac{1}{3}}/c.$$

Remembering that in the case of a normal solution  $n$  is small, being 18/1000, we can develop the last expression in powers of  $n$  as far as the first; and it is evident that as  $p$  the molecular mass possesses the additive property and  $A^{-1}$  possesses the modular property, then  $h$  must also possess the modular property, which is Valson's result.

16. *Second method of finding the Virial Constant for Inorganic Bodies or Solid Bodies in general from the properties of their solutions.*—In this method the compressibility of solutions is used. If a solution could be treated as an ordinary liquid we might attempt to apply the equation of our second method for liquids, namely,

$$l = \frac{4}{3} \left( v_0 \frac{a}{\mu} + \frac{25}{26} R \right) v T;$$

but as the solutions to be dealt with are all aqueous, and as  $a$  for water at ordinary temperatures is quite abnormal, it would be useless to attempt to apply this equation to them; but from the "dimensions" of the physical quantities involved in it, we may make it yield a correct form of empirical equation for solutions. If we neglect the small term  $25R/26$ , and also the difference between  $v$  and  $v_0$  at ordinary temperatures, the equation above suggests the simple form  $l$  varies as  $1/\mu\rho^2$ , that is  $X^{-1}$  varies as  $\mu\rho^2$ , say  $KX^{-1} = \mu\rho^2$ , where  $K$  is a constant, and for water  $KW^{-1} = \mu_w$  the compressibility of water, and as before we have  $X^{-1} = (W^{-1} + nA^{-1})/(1+n)$ . But on account of the rapid alteration of the compressibility of water with pressure, and its anomalous variation with temperature, we must be prepared to admit that the part of the compressibility of a solution due to the water in it is altered from its value in pure water, and is more altered the more the water is compressed in the process of dissolving the salt. Let this compression be measured roughly by the total amount of shrinkage that ensues when 1 molecule of salt is dissolved in 1000 grms. of water, call the shrinkage  $\Delta$ , and let us amend the equation given above to  $KX^{-1} = \mu\rho^2 + f(\Delta)$ . Let suffixes  $a$  and  $b$  attached to symbols refer them to two different bodies, then

$$KX_a^{-1} - KX_b^{-1} = \mu_a\rho_a^2 - \mu_b\rho_b^2 + f(\Delta_a) - f(\Delta_b),$$



but

$$KX_a^{-1} - KX_b^{-1} = Kn(A_a^{-1} - A_b^{-1})/(1+n),$$

$$\therefore Kn(A_a^{-1} - A_b^{-1})/(1+n) = \mu_a \rho_a^2 - \mu_b \rho_b^2 + f(\Delta_a) - f(\Delta_b).$$

Hence, selecting pairs of bodies for which  $\Delta_a = \Delta_b$  approximately, we ought to get  $\mu_a \rho_a^2 - \mu_b \rho_b^2$  proportional to  $cA_a^{-1} - cA_b^{-1}$ , the values of the last expression being obtainable from Table XXXI.

To facilitate the comparison I furnish the following broad statements about  $\Delta$  founded on the study of data as to the molecular volumes of salts, both solid and in solution, given by Favre and Valson (*Compt. Rend.* lxxvii.) Long (Wied. *Ann.* ix.), and Nicol (Phil. Mag. xvi. and xviii.). The modular property applies approximately to shrinkage on solution; the shrinkage of a gramme-molecule of LiCl is 2, and the shrinkage for a gramme-molecule is increased when for Li is substituted

K,	Na,	NH <sub>4</sub> ,	$\frac{1}{2}$ Ca,	$\frac{1}{2}$ Sr,	$\frac{1}{2}$ Ba,
by 8	7	-5	10	11	12;

and when for Cl is substituted

Br,	I,	NO <sub>3</sub> ,	$\frac{1}{2}$ SO <sub>4</sub> ,	$\frac{1}{2}$ CO <sub>3</sub> ,
by 0	0	0	8	14.

After giving the values of  $\mu \rho^2$  in the next table we can proceed with the comparison.

TABLE XXXIV.—Values of  $10^7 \mu \rho^2$ .

	Cl.	Br.	I.	NO <sub>3</sub> .	$\frac{1}{2}$ SO <sub>4</sub> .	$\frac{1}{2}$ CO <sub>3</sub> .
Li .....	432	484	541	457	433	
Na .....	441	496	550	468	444	428
K .....	454	507	557	480	450	437
NH <sub>4</sub> .....	443	493	544	466	442	
$\frac{1}{2}$ Ca .....	464					
$\frac{1}{2}$ Sr .....	497					
$\frac{1}{2}$ Ba .....	521					

The experimental data used are those of Röntgen and Schneider (Wied. *Ann.* xxix.), and those of M. Schumann (Wied. *Ann.* xxxi.) for CaCl<sub>2</sub>, SrCl<sub>2</sub>, and BaCl<sub>2</sub>, in the case of which I calculated the compressibility for the half-gramme molecule according to his result that  $\mu - \mu_w = c\rho$  where  $\rho$  is

percentage of salt, using a value of  $c$  got from the more concentrated solutions.

An inspection of this table shows that  $10^7\mu\rho^2$  possesses the modular property; it gives for instance the following differences for Na and Li, 9, 12, 9, 11, 11, with a mean value 10, and so on for the other metals; the mean values for the metals minus that for Li are:—

Na.	K.	NH <sub>4</sub> .	$\frac{1}{2}$ Ca.	$\frac{1}{2}$ Sr.	$\frac{1}{2}$ Ba.
10	20	8	32	65	89;

and for the negative radicals minus that for Cl:—

Br.	I.	NO <sub>3</sub> .	$\frac{1}{2}$ SO <sub>4</sub> .	$\frac{1}{2}$ CO <sub>3</sub> .
52	105	25	0	—15.

We can now select pairs of bodies for which  $\Delta_a = \Delta_b$  and test if  $\mu_a\rho_a^2 - \mu_b\rho_b^2$  is proportional to  $cA_a^{-1} - cA_b^{-1}$ .

The following are pairs of elements characterized by nearly equal shrinkage on solution with the values of the differences of  $10^7\mu\rho^2$  and of  $cA^{-1}$  and also their ratio.

TABLE XXXV.

Equal shrinkage pair...	K, Na.	$\frac{1}{2}$ Sr, $\frac{1}{2}$ Ca.	$\frac{1}{2}$ Ba, $\frac{1}{2}$ Ca.	Br, Cl.	I, Cl.	NO <sub>3</sub> , Cl.
Mean diff. of $10^7\mu\rho^2$ ...	10	33	57	52	105	25
Mean diff. of $cA^{-1}$ ...	29	1.05	1.85	1.56	3.28	.81
Ratio of differences ...	34	31	31	33	32	31

The agreement here is excellent, as will be seen more clearly if we compare bodies not having equal shrinkage, as K and Li, for which we get the  $10^7\mu\rho^2$  difference 20, the  $cA^{-1}$  difference .90 with a ratio 22, or K and NH<sub>4</sub>, for which the two differences are 12 and 1.05 with a ratio 11.

The agreement above is a verification of the theory of the compressibility of solutions, here barely outlined, and the equation

$$10^7(\mu_a\rho_a^2 - \mu_b\rho_b^2) = 32(cA_a^{-1} - cA_b^{-1})$$

when  $\Delta_a = \Delta_b$  nearly constitutes a second method of getting values of  $cA^{-1}$ ; but we will not use it, as it adds no bodies to our list. It suffices to have partly verified the principles on which the first method is founded by their application to quite

another physical phenomenon, and especially the principle involved in the remarkable equation

$$X^{-1} = (W^{-1} + nA^{-1}) / (1 + n).$$

With the values in Table XXXIII. and that for LiCl, namely, .83, we can obtain the value of  $cA^{-1}$  for any salt whose constituents are to be found in the table, or we can if we like use the actual values in Tables XXX. and XXXI.; we can then calculate  $M^2/cA^{-1}$ , which is proportional to  $M^2l$ , or  $M^2l = CM^2/cA^{-1}$ , where  $C$  is a constant. To connect the values of  $M^2l$  thus found with those previously given absolutely in Table XXV., we must find the value of  $C/c$ , which we can proceed to do in the following manner:—

We have seen (Section 14) that we had better regard the molecule of water as doubled relatively to that of ordinary liquids, and as we have shown that the molecules are paired in ordinary liquids the molecules are doubly paired in water; but it was suggested that the second pairing of the pairs was not attended with any alteration in the parameter of molecular force, and that the only effect of the second pairing was to make the radius of the molecular domain of water  $2^{\frac{1}{3}}$  as large as if water were an ordinary liquid. And, again, in the case of solutions the surface-tensions have been measured at about  $15^\circ \text{C.}$ , whereas for comparison with our previous work they ought to have been measured at  $2T_c/3$ , which for water is about  $150^\circ \text{C.}$  At this temperature the value of the surface-tension of water reduces, according to Eötvös, to about .6 of its value at  $15^\circ \text{C.}$  Hence the equation, which treating water as an ordinary liquid and at  $15^\circ$  we wrote  $\alpha_w = Ww^{\frac{1}{3}}/c$ , ought for double pairing and at  $150^\circ$  to become  $.6\alpha_w = W2^{\frac{1}{3}}w^{\frac{1}{3}}/c$ , and similar statements hold for the equation for  $\alpha$ ; so that values of  $W$ ,  $X$ , and  $A$ , as deduced from measurements at  $15^\circ$ , ought to be reduced by the factor  $.6/2^{\frac{1}{3}}$ , or  $1/2$ , to give the desired values. Now in the case of homogeneous liquids in the equation  $l = cav^{\frac{1}{3}}/m^{\frac{1}{3}}$  giving  $l$  in terms of the megadyne we found a value 5930 for  $c/2$ , with the megamegadyne as unit of force  $c/2 = .00593$ ; and we can use this same value in the case of solutions after we have halved our values of  $A$ , or doubled those of  $cA^{-1}$  so far given; hence using the values of  $cA^{-1}$  so far given we get  $M^2l = .00593M^2/cA^{-1}$ .

Fortunately, a test of this argument is made possible by means of Traube's data for the surface-tension of solutions of certain organic acids and sugars, for which the values of  $\cdot 00593M^2/cA^{-1}$  are given in the following Table, as well as values of  $S$  found by the relation  $M^2l=6S$  (the term  $\cdot 66S^2$  being omitted), and also values of  $S$  calculated from the dynic equivalents in Table XXVI.

TABLE XXXVI.

	Oxalic Acid. (COOH) <sub>2</sub> .	Citric Acid. C <sub>3</sub> H <sub>4</sub> OH(COOH) <sub>3</sub> .	Glycerine. C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub> .	Mannite. C <sub>6</sub> H <sub>8</sub> (OH) <sub>6</sub> .
M <sup>2</sup> l .....	19.4	43.5	33.5	63.0
S=M <sup>2</sup> l/6.....	3.2	7.2	5.6	10.5
S from dynic equiv.	4.2	9.7	5.0	10.0

	Tartaric Acid. C <sub>2</sub> H <sub>2</sub> (OH) <sub>2</sub> (COOH) <sub>2</sub> .	Dextrose. C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> .	Saccharose. C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> .
M <sup>2</sup> l .....	38.9	72.1	112.5
S=M <sup>2</sup> l/6 .....	6.5	12.0	18.8
S from dynic equivalents	7.4	9.6	18.1

The agreement between the two sets of numbers is not all that could be desired, but it is good enough to show that the only part of  $M^2l$  effective in a solution is the linear term in  $M^2l=6S+\cdot 66S^2$ ; and we have already seen that when the molecules of ordinary liquids pair during liquefaction the term  $\cdot 66S^2$  is inoperative in the process, so that there is a certain resemblance in the relations of two paired molecules and those of solvent to those of substance dissolved.

Returning to the inorganic compounds we can now tabulate the absolute values of  $M^2l$ , calculated according to the relation  $M^2l=\cdot 00593M^2/cA^{-1}$ . The manner of calculation is best illustrated by an example, say for KBr; first  $\cdot 83$  is taken as the value for LiCl, and to it are added  $\cdot 90$  and  $1.56$ , taken from Table XXXIII., as the differences for K and Li and for Br and Cl; the square of the molecular weight of KBr is divided by this sum and multiplied by  $\cdot 00593$  to give the tabulated value of  $M^2l$  in terms of the megamegadyne. From the value of  $M^2l$  thus found the dynic equivalent  $S$  is calculated by the relation  $M^2l=6S$ , which has been seen to be appropriate to values of  $M^2l$  obtained from solutions.

TABLE XXXVII.—Values of  $M^2$  and S.

	Cl.		Br.		I.		NO <sub>3</sub> .		$\frac{1}{2}$ SO <sub>4</sub> .		$\frac{1}{2}$ CO <sub>3</sub> .	
	M <sup>2</sup> l.	S.	M <sup>2</sup> l.	S.	M <sup>2</sup> l.	S.	M <sup>2</sup> l.	S.	M <sup>2</sup> l.	S.	M <sup>2</sup> l.	S.
Li ...	12.5	2.1	18.7	3.1	25.7	4.3	17.1	2.8	10.6	1.8		
Na ...	13.7	2.3	20.8	3.5	28.0	4.7	18.8	3.1	12.8	2.1	8.6	1.4
K ...	18.5	3.1	28.3	4.7	32.4	5.4	23.5	3.9	17.2	2.9	12.8	2.1
NH <sub>4</sub> ...	23.0	3.8	27.0	4.5	31.0	5.2	25.0	4.2	17.0	2.8		
$\frac{1}{2}$ Mg ...	10.4	1.7	17.7	3.0	25.1	4.2	15.6	2.6	10.1	1.7		
$\frac{1}{2}$ Ca ...	12.0	2.0	19.4	3.2	26.7	4.5	17.3	2.9				
$\frac{1}{2}$ Sr ...	14.2	2.4	21.8	3.6	29.3	4.9	19.5	3.2				
$\frac{1}{2}$ Ba ...	18.8	3.1	26.4	4.4	33.9	5.6	24.0	4.0				
$\frac{1}{2}$ Zn ...	12.5	2.1	...	...	...	...	...	...	12.6	2.1		
$\frac{1}{2}$ Cd ...	15.7	2.6	23.2	3.9	30.5	5.1	21.0	3.5	16.2	2.7		
$\frac{1}{2}$ Mn ...	11.5	1.9	...	...	...	...	16.8	2.8	11.7	2.0		

To these may be added the following :—

	AgNO <sub>3</sub> .	$\frac{1}{2}$ Pb(NO <sub>3</sub> ) <sub>2</sub> .	$\frac{1}{2}$ CuSO <sub>4</sub> .	$\frac{1}{2}$ FeSO <sub>4</sub> .	$\frac{1}{2}$ NiSO <sub>4</sub> .
M <sup>2</sup> l.....	30.6	26.3	11.5	11.4	12.3
S.....	5.1	4.4	1.9	1.9	2.0

	$\frac{1}{2}$ CoSO <sub>4</sub> .	$\frac{1}{2}$ Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .	$\frac{1}{2}$ Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .	$\frac{1}{2}$ Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .
M <sup>2</sup> l.....	12.7	8.9	12.6	9.6
S.....	2.1	1.5	2.1	1.6

The additive principle holds amongst both sets of numbers except in the case of NH<sub>4</sub>; see for instance the following list of the differences of S for the iodides and chlorides :—2.2, 2.4, 2.3, 2.5, 2.5, 2.5, 2.5. Now we have already seen that the modular principle applies to  $cA^{-1}$  (the modular principle applies when a quantity is given by the addition of modulus to a constant, the additive principle is a special case of the modular in which the constant is zero); the additive principle applies to M the molecular weight: hence it would appear to be a mathematical impossibility that the modular or additive principle should apply also to  $M^2/cA^{-1}$ , rigorously; or, more accurately, if the modular principle applies rigorously to one of the quantities  $cA^{-1}$  and  $M^2/cA^{-1}$  it cannot apply rigorously to the other: but practically we find such relations amongst



the numbers that both are approximately obedient to the modular principle. The case of  $\text{NH}_4$  casts some light on the question, for with it  $cA^{-1}$  shows the same differences in the values of the chloride, bromide, iodide, and nitrate as with the other positive radicals, while  $M^2/cA^{-1}$  does not do so: this case would make it appear that the modular principle applies rigorously to  $cA^{-1}$ , but not so rigorously to  $M^2/cA^{-1}$ .

But leaving out of the count this case of  $\text{NH}_4$ , significant as it is, we can find mean values for the differences of the dynic equivalents of all the metals and Li, and of all the negative radicals and Cl; if we can obtain the absolute value of the dynic equivalent of Li and of Cl, we shall have those for all the metals and radicals. Now from the organic compounds we have already got a value 1·3 for the dynic equivalent of Cl, and hence from the value for LiCl we could obtain that for Li. The value tabulated for LiCl is 2·1, but we can obtain a mean value fairer to all the other bodies by subtracting, for example, from the value for KI the mean difference for K and Li, and for I and Cl; in this way we arrive at a mean value 1·9 for LiCl, from which, taking the value 1·3 for Cl, we should get ·6 for Li. But the refraction-equivalents of the halogens are supposed by Gladstone to be a little larger in inorganic than organic compounds; so that in the light of our previous knowledge of a close parallelism between dynic equivalents and refraction-equivalents it might be safer to assume that the dynic equivalents of Li and Cl in LiCl are in the ratio of their refraction-equivalents in that compound, namely, 3·8 and 10·7. According to this assumption the values for Li and Cl come out ·5 and 1·4, which we will adopt as true and use in the calculation of the dynic equivalents of the elements given in the following Table. These are measured of course as before in terms of that for  $\text{CH}_2$  as unity, and, again, for comparison there are written along with the dynic equivalents the refraction-equivalents in terms of that for  $\text{CH}_2$  as unity, calculated from Gladstone's values (Phil. Trans. 1870).

TABLE XXXVIII.

	Li.	Na.	K.	$\frac{1}{2}$ Mg.	$\frac{1}{2}$ Ca.	$\frac{1}{2}$ Sr.	$\frac{1}{2}$ Ba.	$\frac{1}{2}$ Zn.	$\frac{1}{2}$ Cd.
Dynic equivalent .....	·5	·8	1·6	·3	·55	·9	1·7	·65	1·22
Refraction-equivalent .	·5	·63	1·06	·46	·68	·90	1·04	·67	·9
	Ag.	$\frac{1}{2}$ Pb.	$\frac{1}{2}$ Cu.	$\frac{1}{2}$ Mn.	$\frac{1}{2}$ Fe.	$\frac{1}{2}$ Ni.	$\frac{1}{2}$ Co.	$\frac{1}{3}$ Al.	$\frac{1}{3}$ Fe.
Dynic equivalent .....	2·70	2·0	·6	·5	·6	·7	·8	·2	·8
Refraction-equivalent .	2·06	1·63	·76	·8	·81	·69	·71	·37	·93
	$\frac{1}{3}$ Cr.	Cl.	Br.	I.	NO <sub>3</sub> .	$\frac{1}{2}$ SO <sub>4</sub> .	$\frac{1}{2}$ CO <sub>3</sub> .	$\frac{1}{2}$ CrO <sub>4</sub> .	
Dynic equivalent .....	·3	1·4	2·7	3·8	2·3	1·35	·5	1·7	
Refraction-equivalent .	·7	1·4	2·2	3·6	1·8	1·1	·8	2·4	

Again we see a remarkable parallelism between the dynic and refraction-equivalents of the elements and radicals. Of course there are refinements which will yet have to be made in the calculation of the dynic equivalents, but it is not likely that they will make the parallelism seriously closer.

17. *Meaning of the Parallelism between Dynic and Refraction Equivalents, and general speculations as to the volumes of the atoms and their relation to ionic speeds.*—We are now called upon to consider the meaning of this parallelism which has been demonstrated both for organic and inorganic compounds, and we shall be helped thereto by the very simple theory which I have given of the Gladstone refraction-equivalent (Phil. Mag. Feb. 1889), showing that to a first approximation

$$(n-1)u = \Sigma(N-1)U,$$

where  $n$  is the index of refraction and  $u$  the molecular domain of a substance,  $N$  the index of the matter of an atom, and  $U$  its volume in the molecule. Hence the refraction-equivalent of an element is the product of the refractivity (Sir W. Thomson's name for index minus unity) of the substance of its atom

and the volume of the atom (the volume of the atom being measured in terms of the unit in which the molecular domain, usually called molecular volume, is measured); so that the refraction-equivalent is a function of the two variables only, namely, the volume of the atom and the velocity of light through it. Now we have seen that the expression  $M^2l$ , as a whole, in one aspect appears to be not dependent directly on the molecular mass  $M$ , seeing that  $M^2l$  can be represented in terms of certain quantities which we have called dynic equivalents. Hence, as  $l$  is proportional to  $A$  in our expression  $3Am^2/r^4$  for molecular force, we see that in one aspect molecular force seems to be not directly dependent on the mass of the attracting molecules; and yet, on the other hand, in considering solutions we found that the quantity  $A$  asserted its individuality as separate from the whole expression  $Am^2$ , so that in another aspect there does appear to be a mass action in the attraction of two molecules. However, regarding  $M^2l$  or  $Am^2$  as a whole, the simplest hypothesis we can make about the mutual action of molecules is that it depends most on the size of the molecules. This would make  $Am^2$  a simple function of  $U$ ; so that the dynic and refraction equivalents would have this in common, that they are both simple functions of  $U$ . Suppose, now, that the velocity of light through all matter in the chemically combined state is approximately the same, or that  $N$  is approximately the same for all atoms as constituents of compound molecules, then the refraction-equivalents given by Gladstone are directly proportional to the volumes of the atoms in the combined state, and then the parallelism between dynic and refraction equivalents would mean that  $S$  is nearly proportional to the volume. It is very interesting, therefore, to inquire briefly whether there is any evidence to prove that Gladstone's refraction-equivalents are proportional to the volumes of the atoms; and I think that in Kohlrausch's velocities of the ions in electrolysis we have such evidence. If different solutions, such as those of  $KCl$ ,  $NaCl$ , or  $\frac{1}{2}BaCl_2$ , are electrolysed under identical circumstances, then we know, according to Faraday's law, that each atom of  $K$  and of  $Na$ , and each half-atom of  $Ba$ , may be considered to receive the same charge, so that they acquire their ionic speeds under the action of the same accelerating

force. Accordingly, the ionic speed characteristic of an atom is reached when the "frictional" resistance to its motion is equal to this accelerating force; hence the "frictional" resistance is the same for all atoms, or rather for all electrochemical equivalents. Now the "frictional" resistance will be a function of the velocity of the atom and of its domain (atomic volume) and of its actual volume as well as of the domain and actual volume of the molecule of the solvent; but if water is the solvent in all cases, the only quantities which vary from body to body are the velocity and the domain and volume of the ions, so that we can say

$$\text{"frictional" resistance} = \phi(V, u, U),$$

or

$$V = F(u, U).$$

Now the simplest connexion that one can imagine between the velocity and the domain and volume of the ion is that the velocity will be greatest when the free domain or the difference between the domain and the volume is greatest, or, to be more general, when the difference between the domain and some multiple of the volume is greatest; but if  $N$  is the same for all combined atoms, then  $U$  is proportional to the refraction-equivalent  $q$ . Hence the form of  $F$  is such that it contains  $u - aq$ , where  $a$  is a constant. On studying the experimental data I found that  $a$  might be considered unity, and that  $V$  is a linear function of  $u - q$ . There is a little difficulty in determining with accuracy the domain of an ionic atom in a solution. Nicol, in his work (*Phil. Mag.* xvi., xviii.) on the molecular domains of inorganic compounds in solution, has confined his attention almost entirely to differences of domains, making the assumption suitable to his purpose that the molecular domain of water is unaltered in solutions, whereas we should expect that the greater part of the shrinkage occurring on solution of an inorganic crystal happens in the water, which is far more compressible than the crystal.

Accordingly I take the molecular domains of salts in the solid state, as given by Long in his paper on diffusion of solutions (*Wied. Ann.* ix.), as nearer to the true domain when they are in solution than Nicol's values; but to allow to a certain extent for the change of state on solution, I have assumed

that in each case the water experiences four fifths of the total shrinkage and the dissolved salt one fifth. This is an arbitrary adjustment, and is of no material importance to the comparison to be made except as showing that the point has not been overlooked. In the following Table are given under  $u$  the molecular domains, under  $q$  the molecular refractions (Gladstone's), in the next column their differences; under  $k$  the specific molecular conductivities determined in highly dilute solution by Kohlrausch and shown by him to be equal to the sum of the velocities of the ions in each case. These are taken from his paper (*Wied. Ann.* xxvi.), with a few additions from an earlier one (*Wied. Ann.* vi.). Under  $k$  (calculated) are given values of the conductivity calculated from the equation

$$k = 68 + 2.2(u - q),$$

expressing the linear relation between conductivity or sum of ionic velocities and  $u - q$ .

TABLE XXXIX.

	$u$ .	$q$ .	$u - q$ .	$k$ .	$k$ (calc.).
KI .....	53.5	35.3	18	107	108
KBr .....	44	25	19	107	110
KCl .....	36	18.8	17	105	105
NaI .....	41	32	9	87	88
NaBr .....	32	21.7	10	87	90
NaCl .....	24	15.5	8.5	87	87
LiCl .....	20.5	14.5	6	78	81
$\frac{1}{2}$ MgCl <sub>2</sub> .....	20	14	6	80	81
$\frac{1}{2}$ CaCl <sub>2</sub> .....	22	16	6	81	81
$\frac{1}{2}$ SrCl <sub>2</sub> .....	24	17.5	6.5	83	82
$\frac{1}{2}$ BaCl <sub>2</sub> .....	24	18.6	5.4	86	80
$\frac{1}{2}$ ZnCl <sub>2</sub> .....	23	15.8	7	77	83

The agreement is here such as to prove a true connexion between conductivity and  $u - q$ , the more striking as no relation can be seen between conductivity and  $u$  or  $q$  taken separately. The only bodies I have omitted from Kohlrausch's latter list are the nitrates of some of the above metals and of silver, the hydrogen compounds of the halogens, and the ammonium compounds. These do not give results in harmony with those in the last table, and, indeed, we should hardly expect a compound radical like NO<sub>3</sub> to experience frictional resistance



in the same manner as a single atom like Cl, and as to the hydrogen compounds they form a class by themselves with respect to many physical properties. It will be as well to show the amount of departure in these cases in the following Table :—

	$u$ .	$q$ .	$u-q$ .	$k$ .	$k$ (calc.).
HI .....	56	26	30	327	134
HBr .....	50	16	34	327	142
HCl .....	42	11	31	324	136
KNO <sub>3</sub> .....	47	22	25	98	123
NaNO <sub>3</sub> .....	36	19	17	82	105
NH <sub>4</sub> NO <sub>3</sub> .....	47·5	25·5	22	98	116
NH <sub>4</sub> Cl .....	35·5	22·2	13	104	97

Kohlrausch has pointed out that there is some difficulty in determining the true connexion between ionic velocities and conductivities in the case of the bibasic acids SO<sub>4</sub> and CO<sub>3</sub>, so that we must leave them out of the count for the present.

18. *An Attempt to Determine the Velocity of Light through the substance of the water-molecule.*—In spite of the exceptions, the relation demonstrated in Table XXXIX. is sufficiently striking. To explain it, let us replace  $q$  by its value  $(N-1)U$ ; then, in interpreting the expression  $u-(N-1)U$  as occurring in our expression for the conductivity of a solution, there are two methods of procedure: first, we can assume that  $u-U$ , the free or unoccupied part of the domain, is the most likely to occur, in which case  $N=2$ ; second, that  $u-cU$  occurs in the expression for conductivity, and that  $c$  happens to have the same value as  $N-1$ , on which supposition it would be desirable to determine  $N$ . At present I know of only one way of attempting to find  $N$  or  $v/V$ , the ratio of the velocity of light through free æther to its velocity through the matter of an atom, namely by means of Fizeau's experiment, repeated by Michelson and Morley, on the fraction of its motion communicated by flowing water to light passing through it. Exactly in the manner of my paper (Phil. Mag. Feb. 1889, p. 148) we can estimate the effect of the motion of matter on the light passing through it. Let  $s$  be the distance travelled by light in water flowing through the æther at rest with

a velocity  $\delta$  in the same direction as the light,  $v''$  the mean velocity of light through the flowing water,  $v'$  the mean velocity through still water,  $v$  its velocity through free æther,  $V$  through a molecule of water,  $l$  the mean distance through a molecule, and  $a$  its mean sectional area ; then the total loss of time experienced by a wave of unit area of front or a tube of parallel rays, or, briefly, a ray of unit section in passing through the matter-strewn path  $s$  instead of a clear path in free æther, will be equal to its loss in a molecule multiplied by the number of molecules passed through in the path. This number, when the matter is at rest, is proportional to  $s$ , to  $a$ , and to  $\rho/M$ , or it varies as  $sap/M$  ; but when the matter is in motion it is reduced in the ratio  $1 - \delta/v'' : 1$ . The loss of time in each molecule is found thus :  $l/V$  is the time taken to pass through a molecule, and in this time the molecule moves a distance  $l\delta/V$  and the unit wave-front moves a distance  $l(1 + \delta/V)$ , which in free æther would take a time  $l(1 + \delta/V)/v$  ; so that the loss of time in a molecule is  $l/V - l(1 + \delta/V)/v$ . Hence, the total loss of time in the path  $s$  may be written

$$\frac{ksal\rho}{M} \left( \frac{1}{V} - \frac{1 + \frac{\delta}{V}}{v} \right) \left( 1 - \frac{\delta}{v''} \right).$$

But the loss of time is also  $s/v'' - s/v$ . Equating the two expressions and putting  $M/\rho = u$  and  $al = U$ ,  $v/v'' = n''$ ,  $v/V = N$ , we get

$$u(n'' - 1) = U \left( N - 1 - \frac{\delta}{v} N \right) \left( 1 - \frac{\delta}{v} n'' \right);$$

as  $k$  is equal to 1, seeing that if  $\delta = 0$  and  $U = u$ , then  $N$  must be equal to  $n$ . This equation is the companion to that for still matter, namely,

$$u(n - 1) = U(N - 1).$$

But to allow for deformation of the wave-front in passing through molecules it was shown (Phil. Mag. Feb. 1889, p. 150) that this first approximation might be altered to the form

$$u(n - 1) = U(N - 1) + c\rho,$$

where  $c$  is a constant, and this form was verified, so that we may write

$$\begin{aligned} u(n''-1) &= U \left( N-1 - \frac{\delta}{v} N \right) \left( 1 - \frac{\delta}{v} n'' \right) + c\rho \\ &= U(N-1) \left( 1 - \frac{\delta}{v} \cdot \frac{N}{N-1} - \frac{\delta}{v} n'' \right) + c\rho, \end{aligned}$$

neglecting the term in  $\delta^2$ ;

$$\begin{aligned} \therefore u(n''-n) &= -\frac{\delta}{v} U(N-1) \left( \frac{N}{N-1} + n'' \right) \\ \therefore \frac{n''-n}{n} &= -\frac{\delta}{v} \frac{U(N-1)}{u(n-1)} \cdot \frac{n-1}{n} \left( \frac{N}{N-1} + n'' \right). \end{aligned}$$

Now

$$\frac{n''-n}{n} = \frac{v'-v''}{v''} = -\frac{x\delta}{v''} = -\frac{x\delta}{v'} \text{ approximately,}$$

where  $x$  is the fraction of the water's velocity imparted to the velocity  $v'$  to change it to  $v''$ . Fizeau (*Ann. de Ch. et de Phys.* sér. 3, t. lvii.) found a value  $\cdot 5$  for  $x$ , while Michelson and Morley (*Amer. Journ. Sc.* ser. 3, vol. cxxxi.), in a more extended and accurate series of experiments, found a value  $x = \cdot 43 \pm \cdot 02$ , which we will adopt.  $U(N-1)$  is equal to  $u(n-1)$  measured in the vapour of water, for which Lorenz (*Wied. Ann.* xi.) gives the value  $5\cdot 6$ ; the value for water at  $20^\circ \text{C.}$ , according to his data is  $6$ , and  $n$  is  $1\cdot 333$ , which may also be taken as the value for  $n''$  where it occurs; all these values being substituted in the equation

$$\frac{N}{N-1} = x \frac{n^2}{n-1} \cdot \frac{u(n-1)}{U(N-1)} - n''$$

give the value  $N=9$ . Hence the velocity of light through the water molecule appears to be one ninth of that through free æther. But before we could ascribe any degree of accuracy to this estimate we should need to be surer of the value of  $x$ , whose measurement is attended with great experimental difficulties. It is much to be desired that we had similar measurements for other bodies than water, both liquid and solid, to permit of other estimates of  $N$ , so as to see if it is the same for all compound bodies, and also to decide between the theory here sketched and Fresnel's hypothesis,

that matter carries its own excess of æther with it, so that  $x = (n^2 - 1)/n^2$ , which in the case of water is '437, in excellent agreement with Michelson and Morley's experimental number; but one such agreement is not sufficient to establish an hypothesis founded on such artificial grounds. However, if  $N=9$  then  $N-1=8$ , and we have the electrical specific molecular conductivity  $k=68+2\cdot2(u-8U)$ . It is only a coincidence that this agrees so exactly in form with Clausius's calculation that the number of encounters experienced per second by a molecule of volume  $U$  moving amongst a number of others of volume  $U$  is greater than that experienced by an ideal particle moving under the same circumstances in the ratio  $u:u-8U$ . Further experiment must elucidate the subject-matter of these speculations.

19. *Suggested Relation between the Change in the Volume of an Atom on Combination and the Change in its Chemical Energy.*

—Returning to the idea that the dynic equivalent furnishes a measure of the volume of its atom, we can get a suggestive glimpse into the relation between the volume of an atom and its chemical energy. Kundt has recently (Phil. Mag. July 1888) shown that the velocities of light through the metals (uncombined) are as their electrical conductivities, being in the case of silver, gold, and copper greater than through free æther, and as in this case both  $n-1$  and  $N-1$  are negative, we see that  $(n-1)u$  or  $(N-1)U$  for the metals changes greatly when the metals pass from the combined to the free state. Now this is in strong contrast to the behaviour of the non-metallic elements, which have been shown in the case of O, N, C, S, P, Cl, Br, and I to possess nearly the same values of  $(n-1)u$  in the combined and free states, and the same may perhaps be said of H. Again, in contrast to this approximate inalterability of  $(n-1)u$  for these non-metals we have the fact, already pointed out, that the dynic equivalents of H, O, and N are much smaller in the free than the combined state. If, then, the dynic equivalents give a measure of the volumes of the atoms in both states, we must consider the volumes of free H, O, and N to be smaller than when they are combined, the change of volume corresponding to the change of energy on combination. If this is true, then the elasticity and density

of the non-metallic atoms (or the equivalents of these properties in the electromagnetic or any other theory of light) are so related that although the density changes  $(N-1)U$  remains constant, whereas in the metallic atoms the relation between density and elasticity must be quite different, because, as we have seen,  $(N-1)U$  actually changes sign in some cases.

It would be possible to determine approximate values for the dynic equivalents of the uncombined metals from Quincke's data for the surface-tension of melted metals, and also to get some light on the constitution of salts from his measurements of the surface-tension of melted salts, but these would be most appropriately discussed in connexion with a general study of the elastic properties of solids. I have, however, satisfied myself that the dynic equivalents of the uncombined metals are different from their values in the combined state.

To show the existence of an intimate relation between dynic equivalents and chemical energy we can enumerate the following propositions:—That in the great majority of inorganic compounds the evolution of heat accompanying the passage of an atom from the uncombined to the combined state is almost independent of the nature of the atoms it combines with, similarly the change of dynic equivalent of an atom on combination is almost independent of the nature of the atom it combines with; that in organic compounds, with the exception of the simpler typical forms, the same proposition as this applies both as regards heat and dynic equivalent.

These general remarks are intended to indicate the most hopeful direction for the continuation of these researches to open up new fields; and yet in old fields there is abundance of scope for the application of the law of molecular force towards the acquisition of a knowledge of the structure of molecules, in the elasticity of solids, in the viscosity of gases and of liquids, in the kinetics of solutions, and many kindred subjects.

Melbourne, February 1890.

DISCUSSION (October 28, 1892).

The Discussion on Mr. Sutherland's paper, "*The Laws of Molecular Force*," was reopened by Prof. Perry reading a communication from the President, Prof. Fitzgerald.



He objected to discontinuous theories, especially when Clausius had given a continuous formula much more accurate over a very long range than Mr. Sutherland's discontinuous one. The introduction of Brownian motions without carefully estimating the rates required and energy represented, and without giving any dynamical explanation of their existence, was not satisfactory. It would, he said, be most interesting if Mr. Sutherland would calculate the law of variation of temperature with height of a column of convectionless gas, under conduction alone (for Maxwell thought the inverse fifth power law of molecular attraction was the only one that gave uniformity of temperature under these conditions), and, if necessary, make tests with solid bars. Referring to the statement that molecular attraction at 1 cm. was comparable with gravitation at the same distance, he thought Mr. Boys would question this, and he suggested an *experimentum crucis* of the inverse fourth power law. Both the inverse fourth and inverse fifth power laws assumed symmetry which did not exist. He also took exception to other parts of the paper.

Mr. S. H. Burbury said that, on referring to the author's original paper on which the present one was based, he found that uniform distribution of molecules was assumed. On this supposition the demonstrations given were quite correct, and the potential was a maximum. If, however, the molecules were in motion, the average potential must be less than the maximum, and the deductions in the present paper being based on wrong assumptions were liable to error.

Prof. Ramsay remarked that many statements in the paper on the subject of critical points were very doubtful. Separate equations for the different states of matter were not satisfactory, neither was the artificial division of substances into five classes. The predicted differences in the critical points due to capillarity had not been found to exist. Speaking of the virial equation, he said that hitherto  $R$  had been taken as constant. Considerations he had recently made led him to believe that  $R$  was not constant. The whole question should be reconsidered, regarding  $R$  as a variable.

Mr. Macfarlane Gray said he had been working at subjects similar to those dealt with in Mr. Sutherland's paper, but from an opposite point of view, no attraction being supposed

to exist between molecules. In the theoretical treatment of steam he found that no arbitrary constants were required, for all could be determined thermodynamically. The calculated results were in perfect accord with M. Cailletet's exhaustive experiments except at very high pressures, and even here the theoretical volume was the mean between those obtained experimentally by Cailletet and Battelli respectively.

Prof. Herschel pointed out that Villargéau had discussed the equation of the virial, where the chemical and mechanical energies were not supposed to balance each other. Mr. Sutherland's paper all turns on the existence of such a balance, and he (Prof. Herschel) could not understand why this balancing was necessary.

*Remarks by Dr. GLADSTONE.*

I was naturally attracted to this elaborate and interesting paper by Mr. Sutherland's frequent references to my refraction work, and to the close relation which he sets forth between Dynic and Refraction Equivalents. Dr. Perkin and I had pointed out a similar relation between molecular refraction, dispersion, and magnetic rotation; and I was much interested in the prospect of a fourth series of analogous values. The four series are arranged in the following table on the same principle as in Mr. Sutherland's Table XXVIII., the value of  $\text{CH}_2$  being taken as unity.

Table of Relative Equivalents.

	Dynic.	Refraction.	Dispersion.	Magnetic rotation.
$\text{CH}_2$ .....	1.00	1.00	1.00	1.00
H .....	0.215	0.17	0.12	0.25
C .....	0.57	0.66	0.77	0.50
$\text{CO}''\text{O}'$ .....	1.9	1.47	1.60	0.97
$\text{O}'$ .....	0.6	0.37	0.29	0.26
$\text{NH}_2$ .....	1.23	1.02	1.35	1.20
CN .....	1.35	1.33	1.13	1.01
$\text{NO}_3$ .....	2.2	2.0	2.8	0.84
$\text{S}'$ .....	1.6	1.9	3.5	
Cl .....	1.3	1.3	1.5	1.7
Br .....	1.6	2.0	3.6	3.5
I .....	2.3	3.2	7.7	7.6

A glance at this table will show that there is a certain proportionality between the four columns, but with differences which are certainly beyond the limits of experimental error ; and the value of the figures is seriously impaired by the fact that while hydrogen is sometimes reckoned at 0.215 by what appear to be somewhat arbitrary assumptions, in others of his calculations Mr. Sutherland looks upon it as so small as to be entirely negligible. But in the case of the three optical properties, the analogy does not depend upon the proportionality of the numbers so much as upon the fact that the refraction, dispersion, or magnetic rotation of a compound is the sum of the refraction, dispersion, or magnetic rotation of its constituent atoms, modified to some extent by the way in which they are combined ; and the correspondence is so close in this respect that, in the words of Dr. Perkin and myself, "we find that when a change occurs in the one property it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent." To take one instance out of many, the first and perhaps the second term of a homologous  $\text{CH}_2$  series is found to be somewhat out of range with the higher terms in respect of each of the optical properties. Now it would appear that this is also the case in respect of the Dync equivalent. But the exaltation of effect produced by "double linking" of carbon atoms, which is so very marked in the case of refraction, and still more so in that of dispersion and magnetic rotation, is scarcely apparent in Mr. Sutherland's Dync equivalents, and he has entirely disregarded it in his calculations.

If we were to take  $M^2$ , instead of the Dync equivalent which is deduced from it, we should get different values for each increment of  $\text{CH}_2$  in a homologous series, increasing as the series ascends ; and the same would apply to other radicals. As we deal with the molecular weight  $M$ , and not the square of it, in determining the optical properties, it seemed worth while to reckon what constants we should obtain by the formula  $M$ . When so reckoned, the value for  $\text{CH}_2$  would appear to be the same throughout a homologous series, and also in different series. But it necessitates

starting each series of compounds with an initial constant  $H_2$ ,  $O''O$ ,  $HCl$ ,  $Cl_2$  &c. ; and these constants are of high value. Dr. Perkin was led to adopt the same idea of initial constants in investigating the molecular magnetic rotation. By this method of calculation the effect of "double linking" and of "ring formation" becomes very apparent; but it upsets all proportionality between the Dynic equivalents and the Optical equivalents both in regard to the substances given in the preceding table, and the metals contained in dissolved salts.

Regarding the matter from this point of view, I am disposed to believe that Mr. Sutherland's virial constant ( $l$ ) does represent, more or less correctly, a real property of bodies, and that there is some relationship between it and the three optical properties.

The speculations as to the volumes of the atoms and their relation to ionic speed are very suggestive, and Mr. Hibbert and I hope to make them the basis of some future investigation.

*Discussion on Mr. Sutherland's Paper on the Laws of Molecular Force.* By SYDNEY YOUNG, D.Sc.

Mr. Sutherland's calculations and speculations are based on his law of Force between two similar molecules,

$$3Am^2/r^4,$$

together with Clausius' equation of the virial,

$$\frac{3}{2}pv = \sum \frac{1}{2}mV^2 - \frac{1}{2} \cdot \frac{1}{2} \sum \sum Rr.$$

Mr. Sutherland first discusses the law established by Amagat for gases and by Ramsay and Young for gases and liquids, that at constant volume  $\partial p / \partial T$  is independent of temperature, or, generally, that it is a function of volume only. While admitting the truth of this law for elements and typical compounds such as methane, Mr. Sutherland thinks that for compounds in the liquid state  $\partial p / \partial T$  is slightly variable with the temperature; but Barus has shown that with several liquids, including ether, such variability only becomes evident at extremely high pressures.

Mr. Sutherland then points out that the equation of the virial may be written in the form

$$pv = RTvf(v) + v\phi(v),$$

where  $v\phi(v)$  stands for the internal virial term, which, according to the law of the inverse fourth power, should vary inversely as the volume, or

$$v^2\phi(v) \text{ ought to be constant.}$$

But in the case of ether  $v^2\phi(v)$  is not constant, but diminishes from a supposed limiting value at large volumes to about half this value near the critical volume, below which there is little change. Mr. Sutherland, however, adheres to his law of the inverse fourth power and attempts to explain the discrepancy by the formation of pairs of molecules at small volumes.

A similar variability is to be noticed in the case of carbon dioxide, but with methane and nitrogen, and presumably the other elementary gases,  $v^2\phi(v)$  is considered to be constant, and no pairing is therefore supposed to occur. It may be noticed, however, that the range of volume with carbon dioxide and nitrogen is small, and that in the latter case the values of  $v^2\phi(v)$  are very irregular, while methane is a substance that is very difficult to obtain in a state of perfect purity.

Mr. Sutherland finds it necessary to divide substances into at least five classes :—

1. Elements and typical compounds such as methane (no pairing of molecules).
2. Ethylene (intermediate between 1 and 3).
3. Ordinary compounds (molecules pair at small volumes).
4. Alcohols and water (the pairs pair again).
5. Dissociable substances such as nitrogen peroxide and acetic acid (chemical polymerization ; not considered).

I will refer later to the nature of this "pairing" of the molecules.

Mr. Sutherland then discusses the two virial terms and, beginning with ether and carbon dioxide, shows that from large volumes to near the critical volume each term can be



represented by a comparatively simple formula, and from these he constructs the characteristic equations. For smaller volumes a different equation has to be employed, and a third or intermediate equation is also required.

It is thus necessary to employ three or at least two characteristic equations for each group of substances; and it may be noticed in passing that for ethylene, which is considered to be intermediate between elements and compounds, an additional constant has to be introduced. It is also somewhat curious that while, with this substance, the pairing is only partial at the critical volume, it does not appear to proceed any further at smaller volumes.

Formulae are then given by which the critical temperatures, pressures, and volumes may be calculated from the constants employed in the characteristic equations, and a comparison between the observed and calculated values is given. For ethyl oxide these are as follows:—

	Observed.	Calculated.	$\Delta$
Temperature . . .	194°	199°	5°
Pressure . . .	27·1	29·1	2·2 metres.
Volume . . .	(3·7)	4·7	1 c. c.

Mr. Sutherland seems to consider these differences of temperature and pressure (he does not discuss the errors in volume) as allowable, and here and elsewhere he speaks of an error of 10° or even 20° in the critical temperature as something possible. He also states that capillarity must influence the results. Now this question of the accuracy attainable in the determination of the critical constants appears to me to be one of extreme importance, and I may perhaps refer to some recent work by Mr. G. L. Thomas and myself on the esters. Up to the present we have determined the critical constants of five of these bodies and we have in each case employed two different specimens, great care being of course taken in their purification. The greatest difference we have observed in the critical temperatures of the two samples of the same ester is 0·1° and the greatest difference in pressure is 80 millims.

In the case of ethyl acetate, tubes of different bore were employed in the two determinations, but no effect of capillarity on the critical constants was observable. The actual results for ethyl acetate are :—

	Sample A.	Sample B.
Boiling point (mean) . . .	77°·12	77°·13
Specific gravity at 0° . . .	·92434	·92438
Critical Temperature . . .	250°·1	250°·1
Critical Pressure . . .	28866 mm.	28891 mm.
Internal diameter of tube .	2·04 mm.	1·54 mm.

I think, therefore, that the differences between the observed and calculated results in the case of ether are altogether outside the limits of experimental error, and that either the formula or the constants are not sufficiently satisfactory. With carbon dioxide the differences are much greater, 20° and nearly 20 metres pressure, and I am sure that M. Amagat would not admit any such errors. The critical volume is very much more difficult to determine directly ; but in a paper read before this Society about a year ago I showed how the relative critical volumes of different bodies could be ascertained from the data at lower temperatures, and I then thought that in a few cases the observed critical volumes might be taken as fairly accurate.

Since then M. Mathias has shown that the method of MM. Cailletet and Mathias may be employed with great advantage for the determination of the critical densities of the substances referred to in my paper, and I have much pleasure in acknowledging the accuracy both of the method and of the densities (except, perhaps, in the case of the alcohols) calculated by M. Mathias. Further confirmation of the truth of the law on which the method of MM. Cailletet and Mathias is based has been afforded by M. Amagat with carbon dioxide, and by Mr. Thomas and myself with the five esters alluded to.

In part (6) of his paper Mr. Sutherland discusses Van der Waals' generalizations regarding corresponding temperatures, pressures, and volumes, and the results he arrives at are in

many respects identical with those which I described to the Society last year. As regards the vapour-pressures at corresponding temperatures, we both conclude that for ordinary compounds the law can only be looked upon as a first approximation, but that when the alcohols are compared with other bodies it cannot be regarded as true at all.

Mr. Sutherland does not, however, discuss the question of volumes at any length.

The last point I wish to allude to is the nature of the supposed "pairing" of the molecules in ordinary compounds, but before doing so I must refer to the internal virial constant  $l$ . Mr. Sutherland shows that this constant may be calculated by five more or less independent methods, and that in the few cases where comparison is possible these different methods give fairly concordant results. He then attempts to show that  $l$ , or rather  $M^2l$  ( $M$  being the molecular weight), depends on the composition of the compound and may be calculated by means of what he calls the dynic equivalents,  $S$ , of which the relation to  $M^2l$  is given by the equation

$$M^2l = 6S + \cdot 66S^2.$$

Mr. Sutherland gives values of  $S$  for several elements and groups. By adding together the values of  $S$  for the atoms or groups of atoms in the formula, the dynic equivalent of the compound is obtained, and from this the value of  $M^2l$  and of  $l$  may be calculated, for

$$l = (6S + \cdot 66S^2)/M^2.$$

Mr. Sutherland then points out that if in course of compression a true chemical polymer is formed by the pairing of molecules, the new value of  $l$  should be

$$l' = (6S/2 + \cdot 66S^2)/M^2,$$

or  $l$  is greater than  $\frac{1}{2} l$ .

But in the characteristic equation for compounds the virial constant changes from the limiting value  $\frac{l}{v}$  to  $\frac{l}{2v}$  or  $l' = \frac{1}{2} l$ ; hence Mr. Sutherland concludes that the pairing in

the case of ordinary compounds is not chemical pairing, but he calls it—for the sake of distinction—"physical pairing," and he says "the term  $\cdot 66S^2$  would then appear to have a certain chemical significance."

It is, however, surely remarkable that the "physical pairing" should produce a greater effect on the characteristic equation than true chemical pairing, although it has been shown by Dr. Ramsay and myself (Phil. Mag. Aug. 1887, p. 201) that when chemical pairing does take place, as with nitrogen peroxide and acetic acid, the value of  $\partial p/\partial T$  at constant volume is no longer independent of the temperature.

If Mr. Sutherland's views are correct, we appear to have several different kinds of pairing of molecules:—

1. Chemical pairing, as with nitrogen peroxide, causing the isochors, or lines of constant volume, to be curved.

2. Physical pairing, with no influence on the isochors, but *more* influence on the internal virial term than chemical pairing.

3. Weaker physical pairing of the physical pairs, as in the case of the alcohols. This has not been further studied, but Mr. Sutherland in part (3) of his paper expresses a doubt whether  $\partial p/\partial T$  is really independent of temperature in the case of the alcohols. If, however, this were so, it would appear to follow that curvature of the isochors is caused by true chemical pairing and by weak physical pairing, but not by strong physical pairing.

Mr. Sutherland does not, so far as I can make out, offer any suggestion as to the real nature of this physical pairing, and the idea appears to me to be somewhat speculative and to require further elucidation.

V. *On the Determination of the Critical Density.* By SYDNEY YOUNG, *D.Sc.*, and G. L. THOMAS, *B.Sc.*, *University College, Bristol*.\*

It has been shown by M. E. Mathias (*Compt. Rend.* cxv. p. 35) that the method of determining the Critical Density proposed by MM. Cailletet and Mathias (*Compt. Rend.* cii. p. 1202, civ. p. 1563) gives good results in a considerable number of cases. We have recently investigated some of the thermal properties of five of the lower esters, and find that these substances afford further proof of the truth of the "Law of the Diameter" described by these authors. We therefore think it may be well to give the data illustrating this law, without waiting for the completion of the work on the remaining esters.

The law of the diameter may be briefly explained as follows:—It is well known that if the densities of any substance, both as liquid and as saturated vapour, be mapped as ordinates against the temperatures as abscissæ, they fall on a continuous curve which passes through the critical point. This curve possesses, according to MM. Cailletet and Mathias, the characteristic property that the locus of the middle points of chords parallel to the axis of ordinates is a straight line. If this is so, it follows that the ordinate of the point on the diameter corresponding to the critical temperature gives the critical density.

That the law holds very closely for the esters so far investigated is shown by the results tabulated below. The densities of each substance, both in the state of liquid and of saturated vapour, together with the means of these values, are given for a series of temperatures. The mean densities, calculated from the formula  $D = A + \alpha t$  ( $D$ =density;  $t$ =temperature Centigrade;  $A$  and  $\alpha$  constants depending on the substance) are given in the fifth column, and the differences between these and the observed results in the last column.

\* Read October 28, 1892.



## Methyl Formate.

Temp.	Densities.				
	Observed.			Calc. Mean.	$\Delta \times 1000.$
	Liquid.	Sat. Vap.	Mean.		
40° C.	·9447	·0031	·4739	·4739	0
60	·9133	·0060	·4596	·4596	0
80	·8803	·0105	·4454	·4453	— 1
100	·8452	·0171	·4311	·4310	— 1
120	·8070	·0268	·4169	·4167	— 2
140	·7638	·0412	·4025	·4023	— 2
160	·7136	·0623	·3880	·3880	0
180	·6521	·0943	·3732	·3737	+ 5
190	·6148	·1178	·3663	·3666	+ 3
200	·5658	·1524	·3591	·3594	+ 3
206	·5242	·1862	·3552	·3552	0
210	·4857	·2188	·3522	·3523	+ 1
212	·4549	·2451	·3500	·3508	+ 8
213	·4328	·2681	·3504	·3501	— 3
213·5	·4157	·2865	·3511	·3497	— 14
(Critical) 214·0	.....	.....	.....	·3494	

## Methyl Acetate.

60° C.	·8801	·0031	·4416	·4425	+ 9
80	·8520	·0056	·4288	·4291	+ 3
100	·8222	·0097	·4160	·4156	— 4
120	·7893	·0158	·4026	·4021	— 5
140	·7533	·0246	·3890	·3887	— 3
160	·7133	·0373	·3753	·3751	— 2
180	·6671	·0568	·3620	·3617	— 3
200	·6100	·0866	·3483	·3482	— 1
210	·5741	·1090	·3416	·3414	— 2
220	·5281	·1415	·3348	·3347	— 1
227	·4818	·1775	·3296	·3300	+ 4
230	·4527	·2030	·3278	·3280	+ 2
232	·4226	·2295	·3260	·3266	+ 6
233	·3995	·2520	·3257	·3259	+ 2
(Critical) 233·7	.....	.....	.....	·3255	

Ethyl Formate.					
Temp.	Densities.				
	Observed.			Calc. Mean.	$\Delta \times 1000.$
	Liquid.	Sat. Vap.	Mean.		
60° C.	·8689	·0034	·4362	·4369	+ 7
80	·8410	·0061	·4236	·4239	+ 3
100	·8112	·0103	·4108	·4102	- 6
120	·7796	·0166	·3981	·3980	- 1
140	·7448	·0256	·3852	·3850	- 2
160	·7058	·0388	·3723	·3720	- 3
180	·6610	·0575	·3592	·3591	- 1
200	·6067	·0862	·3464	·3461	- 3
210	·5724	·1075	·3400	·3396	- 4
220	·5290	·1380	·3335	·3331	- 4
225	·5014	·1585	·3300	·3299	- 1
230	·4635	·1890	·3262	·3266	+ 4
233	·4281	·2198	·3240	·3247	+ 7
234	·4117	·2353	·3235	·3240	+ 5
(Critical) 235·3	.....	.....	.....	·3232	
Ethyl Acetate.					
80° C.	·8245	·0035	·4140	·4144	+ 4
100	·7972	·0062	·4017	·4019	+ 2
120	·7683	·0103	·3893	·3894	+ 1
140	·7378	·0165	·3771	·3769	- 2
160	·7033	·0258	·3645	·3644	- 1
180	·6653	·0388	·3520	·3519	- 1
200	·6210	·0580	·3395	·3394	- 1
220	·5648	·0891	·3270	·3269	- 1
230	·5281	·1130	·3206	·3206	0
240	·4778	·1500	·3139	·3144	+ 5
245	·4401	·1800	·3106	·3103	- 3
247	·4195	·1995	·3095	·3100	+ 5
249	·3893	·2290	·3091	·3088	- 3
(Critical) 250·1	.....	.....	.....	·3081	
Methyl Propionate.					
80° C.	·8408	·0032	·4220	·4224	+ 4
100	·8137	·0057	·4097	·4100	+ 3
120	·7852	·0096	·3974	·3976	+ 2
140	·7553	·0153	·3853	·3852	- 1
160	·7222	·0235	·3728	·3727	- 1
180	·6841	·0355	·3598	·3603	+ 5
200	·6445	·0524	·3484	·3479	- 5
220	·5938	·0781	·3360	·3355	- 5
230	·5635	·0966	·3300	·3293	- 7
240	·5220	·1240	·3230	·3231	+ 1
245	·4975	·1415	·3195	·3200	+ 5
250	·4655	·1675	·3165	·3169	+ 4
253	·4401	·1890	·3145	·3150	+ 5
255	·4151	·2120	·3136	·3138	+ 2
256	·3977	·2295	·3136	·3131	- 5
(Critical) 257·4	.....	.....	.....	·3123	

The constants for the formula  $D = A + at$  are :—

Substance.	A.	a.
Methyl Formate . . .	·5025	—·0007155
Methyl Acetate . . .	·4839	—·0006740
Ethyl Formate . . .	·4759	—·0006490
Ethyl Acetate . . .	·4644	—·0006250
Methyl Propionate . .	·4721	—·0006210

The critical densities of the five esters, obtained by the method of diameters, are :—

Methyl Formate . . . . .	·3494
Methyl Acetate . . . . .	·3255
Ethyl Formate . . . . .	·3232
Ethyl Acetate . . . . .	·3081
Methyl Propionate . . . . .	·3123

From the differences between the observed and calculated mean densities it may be concluded that, though there may be in some cases a slight indication of curvature, it is far too small to affect the determination of the critical densities of these substances.

## VI. *On the Determination of the Critical Volume.*

By SYDNEY YOUNG, D.Sc., *University College, Bristol*.\*

ABOUT a year ago I read a paper before the Physical Society † on the “Generalizations of Van der Waals regarding Corresponding Temperatures, Pressures, and Volumes;” and at the close of the paper, after calling attention to the extreme difficulty attending the determination of the critical volume, I described a method by which the relative critical volumes of various substances could be ascertained. At that time it appeared to me that the direct determinations of the critical volumes of benzene, fluorbenzene, chlorobenzene, and acetic acid were probably approximately correct; and I was supported in this view by the fact that the ratios of the observed volumes

\* Read October 28, 1892.

† Proc. Physical Soc. vol. xi. p. 233.

to that of fluorbenzene were practically identical with the ratios obtained by the graphical method then described.

I therefore assumed that the observed critical molecular volume of fluorbenzene was correct, and calculated the volumes of the other substances from their ratios to that of fluorbenzene, and gave these values as the probable critical molecular volumes of the other eleven substances. It was observed, however, that the critical volumes of the three alcohols and of ether obtained by this method were considerably lower than those previously deduced by Dr. Ramsay and myself, and were also lower than those calculated by M. Guye (*Compt. Rend.* cxii. p. 1257). Finally, I pointed out that if these values are taken as correct it would appear that the ratio of the actual critical density to the theoretical (for a "perfect" gas) is for many substances about 4.4.

Since then, M. E. Mathias has shown (*Compt. Rend.* cxv. p. 35) that the critical densities of the substances referred to in my paper may be determined by the method described by MM. Cailletet and Mathias (*Compt. Rend.* cii. p. 1202, civ. p. 1563). The method has also been found by M. Amagat to give excellent results with carbon dioxide, and by Mr. G. L. Thomas and myself with five of the lower esters; and I have therefore much pleasure in acknowledging the correctness both of the method (except, perhaps, in the case of the alcohols) and of the critical densities calculated by M. Mathias, and I have no hesitation in accepting these values in place of those previously adopted.

I have myself made an independent calculation of the critical densities of the twelve substances by this method, and the results I have obtained are practically identical (except in the case of the alcohols) with those given by M. Mathias.

The law of MM. Cailletet and Mathias may be described very briefly as follows:—The means of the densities of any substance in the state of liquid and of saturated vapour, when mapped against the temperature, fall on a straight line. I quite agree with M. Mathias that in the great majority of cases the verification of the law is perfect; but with the three alcohols, especially methyl alcohol, there appears to me to be very decided curvature, too pronounced to be neglected,

and I think it must be admitted that these substances behave exceptionally in this as in many other respects.

M. Mathias admits that at low temperatures the alcohols cease to follow the law ; but he is satisfied with the agreement between the observed and calculated mean densities for a range of  $200^{\circ}$  from the critical point. The constants employed by M. Mathias for ethyl alcohol can be ascertained from his paper, and I give below the mean densities calculated from these constants, together with those calculated from the observed molecular volumes given in my paper (*loc. cit.*).

The constants for the formula  $D=A+\alpha t$  are:—

$A=.4149$ ,  $\alpha=-.0005576$ ,  $t$ =temperature (Centigrade).

Means of Densities of Liquid and Saturated Vapour.

Temperature, Centigrade.	Observed.	Calculated.	$\Delta \times 1000$ .
22.4	.3937	.4024	+87
39.45	.3865	.3929	+64
65.75	.3749	.3782	+33
89.7	.3636	.3649	+16
105.55	.3560	.3560	0
128.1	.3442	.3435	- 7
144.65	.3350	.3342	- 8
151.65	.3309	.3303	- 6
163.8	.3240	.3233	- 4
187.9	.3104	.3101	- 3
206.35	.2998	.2998	0
221.35	.2899	.2915	+16
229.2	.2850	.2871	+21
234.3	.2811	.2843	+32
238.9	.2781	.2817	+36
243.1	.....	.2793	

From the above differences it will, I think, be concluded that there is considerable curvature of the “diameter” in the case of ethyl alcohol, and with methyl alcohol it would be still more marked.

I now give a revised table of the critical densities and volumes of the twelve substances, adding, for the sake of convenience, the critical temperatures and pressures. The critical densities are those calculated by M. Mathias ; but in the case of the alcohols I give also the values which I have



*Critical Constants.*

Substance.	Temperature, Cent.	Pressure, in millims.	Density.	Vol. of 1 gram.	Mol. Vol.	Ratios of Mol. Vol. to that of Fluorbenzene.	
						New.	Old.
Fluorbenzene .....	286.55	33910	.8543	2.822	270.4	.....	.....
Chlorobenzene .....	360	33910	.8661	2.731	306.5	1.133	1.125
Bromobenzene .....	397	33910	.4857	2.059	322.4	1.192	1.180
Iodobenzene .....	448	33910	.5838	1.713	348.4	1.289	1.277
Benzene .....	288.5	36395	.8037	3.293	256.3	.948	.944
Carbon Tetrachloride .....	283.15	34180	.5558	1.799	276.1	1.021	1.010
Stannic Chloride .....	318.7	28080	.7423	1.347	349.3	1.292	1.290
Ether .....	194.4	27060	.2631	3.801	280.7	1.038	1.047
Acetic Acid .....	321.6	43400	.3514	2.846	170.3	.630	.630
Methyl Alcohol. M. ....	240.0	59760	.2784	3.592	114.7	.424	.440
" " Y. ....	"	"	.2705	3.697	118.0	.437	
Ethyl Alcohol. M. ....	243.1	47850	.2793	3.580	164.3	.608	.620
" " Y. ....	"	"	.2750	3.636	166.9	.617	
Propyl Alcohol. M. ....	263.7	38120	.2778	3.600	215.5	.797	.800
" " Y. ....	"	"	.2752	3.634	217.6	.805	

obtained by the same method, taking into account the curvature of the "diameter." The critical volumes of a gram and molecular volumes are calculated from the densities. The last two columns contain the ratios of the new critical molecular volumes to that of fluorbenzene, together with the ratios given on p. 184 of my previous paper and obtained by the graphical method there described. It will be seen that these ratios show satisfactory agreement.

As regards the alcohols it will be noticed that, if the curvature of the diameter is taken into account, the critical densities are lower and the volumes higher; also that the ratios of the critical molecular volumes to that of fluorbenzene agree better with those obtained by the graphical method.

It may be pointed out that if the generalizations of Van der Waals were strictly true, the angular coefficients ( $\alpha$ ) of the diameters of different substances should be directly proportional to their critical densities and inversely proportional to their absolute critical temperatures, or that for any substance

$$\alpha = \text{const.} \times \frac{D}{T}; \text{ or } \frac{\alpha T}{D} = \text{const.}$$

I have calculated the values of this "constant" for the substances mentioned in this paper (with the exception of methyl and propyl alcohol) and for the five esters studied by Mr. G. L. Thomas and myself.

Substance.	$\frac{\alpha T}{D}$ .	Substance.	$\frac{\alpha T}{D}$ .	Substance.	$\frac{\alpha T}{D}$ .
Fluorbenzene	·932	Carbon Tetrachloride	·899	Methyl Formate...	·997
Chlorobenzene	·953	Stannic Chloride ..	·988	Methyl Acetate ...	1·047
Bromobenzene	·957	Ether .....	·972	Ethyl Formate ...	1·061
Iodobenzene	·957	Acetic Acid.....	·993	Ethyl Acetate .....	1·055
Benzene .....	·921	Ethyl Alcohol* .....	1·030	Methyl Propionate	1·021

It can hardly be said that there is more than a rough approximation to constancy in the values of  $\frac{\alpha T}{D}$ .

I have recalculated the ratios of the actual to the theoretical critical densities, and the results are given in the following table:—

\* M. Mathias' value of  $\alpha$ .

Fluorbenzene . . . . .	3·79	Stannic Chloride . . . .	3·75
Chlorobenzene . . . .	3·78	Ether . . . . .	3·82
Bromobenzene . . . .	3·81	Methyl Alcohol . . . .	4·52
Iodobenzene . . . . .	3·79	Ethyl Alcohol . . . . .	4·02
Benzene . . . . .	3·71	Propyl Alcohol . . . .	4·02
Carbon Tetrachloride.	3·66	Acetic Acid . . . . .	5·00

The first eight numbers agree fairly well; and it may be stated that *for many substances the ratio of the actual critical density to the theoretical density (for a perfect gas) is about 3·8*. The alcohols, notably methyl alcohol, and acetic acid, form exceptions to this law, and in the case of the esters the ratios (3·89 to 3·95) are rather high.

22 {  
VII. *On the Boiling-points of different Liquids at Equal Pressures.* By SYDNEY YOUNG, D.Sc., Professor of Chemistry, University College, Bristol\*.

EARLY in the present year, M. E. Colot (*Compt. Rend.* cxiv. p. 653) described a relation between the boiling-points of any two liquids under equal pressures, which may be shortly described as follows.

If  $t$  and  $\theta$  are the temperatures of the two substances at any pressure, then

$$t = A\theta + B,$$

where  $A$  and  $B$  are constants depending on the nature of the liquids.

The constants given by M. Colot refer to Centigrade temperatures, but for the purpose of this paper it is better to employ absolute temperatures. In this case  $A$  remains unaltered, but  $B$  has a different value.

There are certain cases in which  $B=0$  (for absolute temperatures), and the equation then becomes

$$t = A\theta \text{ or } \frac{t}{\theta} = A.$$

This is identical with the equation given by Dr. Ramsay and myself (*Phil. Mag.* Jan. 1886, p. 33) for certain closely related substances such as ethyl chloride and bromide or chlorobenzene and bromobenzene, and I have shown that it holds good for the four halogen derivatives of benzene.

\* Read October 28, 1892.

For bodies which are not closely related we proposed an equation which may be written

$$R = R_0 + ct,$$

where  $R$  is the ratio of the absolute temperatures of the two substances at any pressure  $p$ ,  $R_0$  is the ratio at such a pressure that the temperature of the second liquid  $= 0^\circ \text{C.}$ , and  $t$  is the Centigrade temperature of the same liquid at the pressure  $p$ .

The second terms of the two formulæ ( $B$  in that of M. Colot and  $ct$  in the one just mentioned) are not equivalent, but they both serve to bring the calculated results pretty well within the limits of experimental error, though not in all cases for an indefinite range of pressure.

I have calculated the constants for both formulæ for eleven pairs of liquids of which the boiling-points, at a number of equal pressures, are given in Table I.

The constants for the eleven pairs of substances are given in Table II.

It will be noticed that the constants  $B$  and  $c$  are always of opposite sign, and that as regards magnitude they both fall, with one exception, in the same order.

In Table III. I have given the differences between the calculated and observed temperatures for each pair of liquids and for both formulæ. I have in each case taken the greatest available range of pressure to make the test as searching as possible.

It will be seen that when the constants  $B$  or  $c$  are very small, both formulæ give good results, and either of them may be employed for a very wide range of pressure. For the equation  $R = R_0 + ct$  the agreement is good in the case of methyl acetate and benzene, although  $c$  has a comparatively high value, but when one of the two liquids is water, an alcohol, or acetic acid, the differences are decidedly greater.

The applicability of the formula  $t = A\theta + B$  seems to depend more directly on the magnitude of the constant  $B$ ; there is, indeed, a rough proportionality between the constants and the mean differences given at the foot of Table III. It is quite clear that in the last five cases the relation between the boiling-points is represented by a curve and not a straight line, and a slight tendency to curvature is noticeable even in some of the other comparisons.

TABLE I.  
Boiling-Points, Centigrade.

Pressure in mm.	Benzene. $C_6H_6$ .	Fluor- benzene. $C_6H_5F$ .	Carbon Tetra- chloride. $CCl_4$ .	Stannic Chloride. $SnCl_4$ .	Ether. $(C_2H_5)_2O$ .	Methyl Acetate. $CH_3COOCH_3$ .	Ethyl Acetate. $C_2H_5COOCH_3$ .	Water. $H_2O$ .	Methyl Alcohol. $CH_3OH$ .	Ethyl Alcohol. $C_2H_5OH$ .	Acetic Acid. $CH_3COOH$ .
10	.....	-12.35	-20.5	8.8	.....	.....	-14.0	11.25	-16.25	-2.3	17.2
50	11.8	+16.3	+7.95	39.6	.....	-4.05	+12.8	38.3	+8.6	+22.2	47.4
100	26.25	30.9	22.25	55.35	-12.1	+9.05	26.35	51.6	20.9	34.5	62.7
200	42.4	47.25	38.7	73.0	+1.6	23.45	41.6	66.45	34.5	48.1	79.7
400	60.8	65.75	57.2	93.0	17.4	39.85	59.0	83.0	49.45	62.95	98.7
760	80.25	85.1	76.75	114.2	34.45	57.25	77.1	100.0	64.8	78.3	118.2
1000	89.5	94.3	85.95	124.25	42.45	65.3	85.9	107.95	72.0	85.4	127.35
2000	115.85	120.25	112.3	152.55	65.05	87.9	110.05	129.55	91.6	104.9	152.8
4000	146.0	150.8	143.3	186.0	91.55	114.5	138.25	154.25	113.8	127.2	182.1
7000	175.05	179.8	172.95	217.75	116.6	139.3	164.75	176.9	134.3	147.8	209.0
10000	196.05	200.6	194.4	240.55	134.6	157.3	183.95	192.8	148.8	162.55	227.8
15000	222.1	226.7	220.8	269.1	157.0	179.55	207.75	212.25	166.4	180.75	250.6
20000	242.2	246.7	241.3	290.9	174.55	196.7	225.75	227.3	179.9	194.7	268.15
25000	258.8	263.0	258.3	309.1	189.1	210.7	240.4	239.9	191.0	206.2	282.45
30000	272.9	277.0	272.7	.....	.....	222.75	.....	250.5	200.5	216.05	294.8
35000	285.25	.....	285.2	.....	.....	233.2	.....	259.9	208.9	224.7	305.7
40000	.....	.....	.....	.....	.....	.....	.....	268.35	216.15	232.3	315.4



TABLE II.

Substances.	For $t=A\theta+B$ .			For $R=R_0+ct$ .		
	A.	B.	$t=\text{absolute temp. of}$	$R_0$ .	$c$ .	$t=\text{Centigrade temp. of}$
$\text{CH}_3\text{COOC}_2\text{H}_5$ and $\text{CH}_3\text{COOCH}_3$ .....	1.0620	—	$\text{CH}_3\text{COOC}_2\text{H}_5$	1.0611	+0.000035	$\text{CH}_3\text{COOCH}_3$
$\text{C}_6\text{H}_6$ and $(\text{C}_2\text{H}_5)_2\text{O}$ .....	1.1556	—	$\text{C}_6\text{H}_6$	1.1483	+0.000160	$(\text{C}_2\text{H}_5)_2\text{O}$
$\text{C}_6\text{H}_6$ and $\text{C}_6\text{H}_5\text{F}$ .....	1.0018	—	$\text{C}_6\text{H}_6$	0.9838	+0.000313	$\text{C}_6\text{H}_5\text{F}$
$\text{C}_6\text{H}_6$ and $\text{CCl}_4$ .....	0.9843	+	$\text{C}_6\text{H}_6$	1.0138	—0.000500	$\text{CCl}_4$
$\text{SnCl}_4$ and $\text{CCl}_4$ .....	1.0758	+	$\text{SnCl}_4$	1.1130	—0.000710	$\text{CCl}_4$
$\text{H}_2\text{O}$ and $\text{C}_2\text{H}_5\text{OH}$ .....	1.0953	—	$\text{H}_2\text{O}$	1.0552	+0.000777	$\text{C}_2\text{H}_5\text{OH}$
$\text{CH}_3\text{COOCH}_3$ and $\text{C}_6\text{H}_6$ .....	0.8637	+	$\text{CH}_3\text{COOCH}_3$	0.9459	—0.001410	$\text{C}_6\text{H}_6$
$\text{SnCl}_4$ and $\text{CH}_3\text{COOH}$ .....	1.1349	—	$\text{SnCl}_4$	0.9585	+0.003000	$\text{CH}_3\text{COOH}$
$\text{C}_6\text{H}_6$ and $\text{HO}_2$ .....	1.2528	—	$\text{C}_6\text{H}_6$	0.8885	+0.0006130	$\text{H}_2\text{O}$
$\text{CCl}_4$ and $\text{CH}_3\text{OH}$ .....	1.3872	—	$\text{CCl}_4$	0.9840	+0.0008370	$\text{CH}_3\text{OH}$
$\text{C}_6\text{H}_6$ and $\text{C}_2\text{H}_5\text{OH}$ .....	1.3649	—	$\text{C}_6\text{H}_6$	0.9441	+0.0008030	$\text{C}_2\text{H}_5\text{OH}$



It is obvious, however, that by taking a smaller range of pressure—say from the lowest to 2000 millim., or from 4000 millim. to the highest pressure, and by altering the constants, a very much better agreement would be obtained. Extrapolation beyond the limits of pressure chosen would, however, introduce very large errors indeed.

In conclusion it may, I think, be stated that in a great number of cases, including pairs of widely different bodies, the formula of Ramsay and Young gives better results than that of M. Colot; the latter, which is very convenient, may, however, be employed, even for very wide ranges of pressure, when the constant B is small, and for small ranges of pressure when B is large.

VIII. *Separation and Striation of Rarefied Gases under the Influence of the Electric Discharge.* By E. C. C. BALY\*.

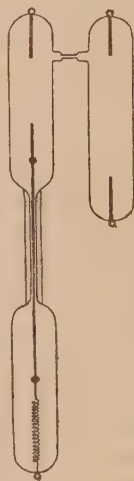
SOME time ago, on examining with a spectroscope a vacuum-tube which happened to contain a small quantity of hydrogen, during the passage of the electric spark I noticed that the hydrogen lines, while strongly visible in the negative glow, could not be seen in the body of the tube. The hydrogen appeared to be, in fact, withdrawn from the tube and collected about the negative pole. Finding the same result in a tube which I fitted up for the purpose, it appeared to me to point to a separation of the gases in the tube; and I determined to make a series of experiments with a view to investigating the matter and the behaviour generally of different gases under similar conditions.

The tubes I employed were about 9 inches long and  $\frac{3}{4}$  inch internal bore. The electrodes were of aluminium wire, and, except in certain cases to which I shall refer, about  $1\frac{1}{2}$  inch in length. Two of these tubes were connected to the pump at the same time, one direct and the other through tubes for the absorption of mercury vapour; so that in all the experiments results were obtained in the presence and in the absence of mercury vapour. Gas-generators, fitted with

\* Read February 10, 1893.

purifying and drying apparatus, were connected so as to allow of varying quantities of the particular gases under examination being admitted to the tubes as might be required. The pump, I may mention, was a modified form of the Geissler mercury-pump, to which I was able to attach an automatic apparatus for working it—a very great saving of labour. Measurements of the vacua were obtained by means of an ordinary barometer-gauge, and varied from 15 millim. to  $\frac{1}{4}$  millim.

I first worked with varying quantities of carbon dioxide and hydrogen. On using certain mixtures of these gases exhausted to about  $\frac{3}{4}$  millim., when the current was first passed a white glow appeared throughout the tube, no striæ being visible, giving a mixed spectrum of the two gases. After a few seconds the negative glow changed to a pink colour, and well-defined striæ, whiter than the preceding glow, began to appear. On watching this change with the spectroscope, the hydrogen lines in the tube were seen to become fainter and gradually to disappear, leaving only the spectrum of carbon dioxide, while those in the negative glow became extremely brilliant. The current was then stopped, and the tube allowed to rest for about an hour, when, the current being passed again, the same phenomenon precisely occurred. Judging that if this were caused by actual separation of the two gases, it ought to be possible to fractionate out the hydrogen into another tube, I endeavoured for a long time unsuccessfully to do so; but at length succeeded by using a double tube of the shape shown in the figure. The longer of the tubes consisted of two chambers joined by capillary tubing, the smaller tube being connected to one of these by a narrow neck capable of being sealed off. Both tubes were furnished with electrodes. One of those in the large tube was sufficiently long to project through the capillary into the second chamber, and being connected at its base to the sealed platinum by a weak spiral wire



could be dropped sufficiently far to touch the opposite electrode. This rod was made of copper, as being heavier than aluminium. It fitted the capillary fairly well, and was furnished with small stops of cotton-wool in order to close the capillary, and thus prevent as much as possible the diffusion of the gases. The tube, after being filled with the gases carbon dioxide and hydrogen, was exhausted and sealed from the pump. The copper rod was caused to touch the opposite electrode, and the current was passed so as to make the whole of the long tube the negative pole and the electrode at the lower end of the smaller tube the positive. The current was continued for a considerable time, when the connecting-neck between the tubes was sealed off and the copper rod shaken back to the stop. On comparing the spectra of the two tubes, it was found that the small tube (containing the positive pole) showed only a trace of hydrogen, while the other showed it brilliantly.

This, I think, may be considered a proof of an actual though not complete separation of the two gases.

I then tried hydrogen mixed with many other gases—amongst them nitrogen, carbon monoxide, sulphur dioxide, iodine, and mercury vapour; and in every case, without exception, I found that the hydrogen was collected about the negative pole in exactly the same manner as I have particularized.

I proceeded to examine mixtures of other gases. With carbon monoxide and carbon dioxide, the carbon monoxide is separated out and appears in the negative glow. With carbon dioxide and nitrogen the carbon dioxide is separated out, while the nitrogen remains in the tube, the separation being remarkably distinct. In this case it is the heavier gas which is separated out; and the same is found with carbon dioxide and sulphur dioxide, the sulphur dioxide appearing in the negative glow.

It would thus appear that the separation of two gases does not depend on their relative molecular weights. On examining a tube of air, however, the components of which are of fairly equal molecular weight, a separation was found to be very difficult, and only occurred after carrying the exhaustion to a much higher point than was usually necessary. The



nitrogen remained in the tube, and the negative glow gave a spectrum presumably oxygen; I say presumably, for I am unable to see what else it can be. I was unable to produce the same spectrum in a tube with oxygen, but I was prevented from proceeding further. The spectra of oxygen Professor Schüster has shown to be very varied under different conditions. Is it not possible that the two spectra in an oxygen tube, the banded one in the negative glow, and the bright-line one in the rest of the tube, may be due to separation of two gases?

From these experiments it is evident that when the electric current is passed through a rarefied mixture of two gases, a process similar to electrolysis is set up, one of the gases being separated out and collected about the negative pole, the other gas remaining in the tube; the proof being that the gas separated out may be fractionated into another tube by the method I have above described. In pursuing these experiments I was struck by the apparent close connexion between separation and striation; that is to say, I found strongly marked striæ when there was good separation, and feeble striæ when the separation was difficult; I also found that the first appearances of these phenomena were coincident, the formation of striæ being always the sign of the commencement of separation. There were no exceptions to this, the action in all the tubes I made being the same.

It was evident to me that, if the connexion were real and the separation of the gases could in some way be prevented, by avoiding the negative glow, striæ would not be formed. I accordingly made a tube the negative pole of which did not protrude from the little glass collar in which it was placed, the positive electrode being made as usual. The tube was filled with a mixture of hydrogen and carbon dioxide and exhausted. At a pressure of 24 millim. the current was passed; instead of a negative glow appeared a little bunch of light about  $\frac{1}{8}$  inch below the negative point. If this bunch of light impinged on the side of the tube, the glass became strongly phosphorescent. At 4 millim. there was no bunch of light or negative glow; there was no sign of any striæ, the tube giving a spectrum of hydrogen and carbon dioxide, and no evidence of separation. I then reversed the current; imme-

diately striæ formed, separation began and became well-marked.

I tried various mixtures of gases and always obtained the same result, viz., that when the negative glow was avoided by the use of the minute electrode point, neither striæ nor separation occurred, but in reversal of the current strongly marked striæ and good separation.

My next step was to experiment with a pure vapour, which, if my contention be correct, should not striate. It is known that a tube of pure mercury vapour does not stratify. I prepared a tube for the purpose, one end of which was connected with the pump and the other with a bulb containing mercury. After exhaustion, I strongly heated the tube and boiled the mercury, which thus distilled through the tube. On passing the current, as I expected, no striæ appeared, but simply a beautiful phosphorescence throughout the tube, giving a spectrum of pure mercury only. On ceasing to boil the mercury and allowing the tube to cool, a small quantity of other gas was necessarily drawn in from the pump. Immediately striæ began to appear, beginning at the end of the tube connected with the pump; the negative glow changed at the same time and gave a spectrum containing other lines in addition to those of mercury, thus strongly confirming my previous conclusion.

Thinking that possibly the absence of striæ might arise, not from the purity of the mercury vapour, but from its molecules being monatomic, I repeated the experiment with pure vapours of iodine, sulphur, arsenic, and mercuric iodide, which are not monatomic. The result was in each case precisely the same—the tube while heated showing no striæ, but on cooling both striæ and separation.

Wishing if possible to obtain a pure gas which did not stratify at *ordinary* temperatures, I made many attempts to prepare a tube of pure hydrogen. The nearest approach to success was with hydrogen prepared from pure caustic potash and aluminium. The gas was then absorbed by red-hot palladium, which was re-heated in the vacuum. On passing the current, the tube showed an even phosphorescent light throughout, with a very faint line of the most delicate striæ, very difficult to distinguish. The striæ did not become any

plainer on carrying the exhaustion to a considerably higher point. I think it may be safely assumed that a tube of perfectly pure hydrogen would not striate at all.

From the foregoing results I think the following conclusions may be drawn :—

First, that when an electric current is passed through a rarefied mixture of two gases, one is separated from the other and appears in the negative glow.

Second, that striæ are caused by the separation of the two gases, and do not occur in a single pure gas or vapour.

#### DISCUSSION.

Mr. Crookes said :—

In my Inaugural Address delivered before the Institution of Electrical Engineers on January 15th, 1891, I showed some experiments and gave reasons which had led me to believe that the stratifications seen when a high-tension current is passed through a rarefied gas were due to the gas not being homogeneous. I took the case of hydrogen in a vacuum-tube at a pressure of 2 millim. The gas was prepared from zinc and sulphuric acid, and was purified and dried in the usual manner, but with no special precautions against impurities. The exhaustion was effected with a mercury pump, thus leaving mercury vapour in the residual hydrogen.

The stratifications are tri-coloured—blue, pink, and grey. Next the negative pole is a luminous layer; then comes a dark interval, or Faraday's dark space; and after this are the stratifications, the front component of each group blue, the next pink, and the third grey. The blue discs are somewhat erratic. At a certain stage of exhaustion all the blue components of the stratification suddenly migrate to the front, forming one bright blue disc, and leaving the pink and grey components by themselves. When the tube contains a compound gaseous residue of this kind, the form of stratifications can be very considerably altered by varying the potential of the discharge.

.... That the alteration depends simply on the difference of potential, the following experiment pretty clearly shows:—Take a tube giving on the coil the coloured stratifications usually attributed to the presence of residual hydrogen, but which I find is *due to a mixture of hydrogen, mercury, and*

*hydrocarbon vapours*. Then, by altering the break so as to produce frequent discharges of lower potential, the stratifications gradually change in shape and become all pink; again, altering the break, so as to send less rapid discharges at a much higher potential, once more we get the coloured stratifications. When in this state, if we introduce a water resistance into the circuit, so as to damp down the potential, exactly the same thing happens. *The blue disk is caused by mercury*; its spectrum is that of mercury only, without even a trace of the bright red line of hydrogen. Experiments not yet finished make it very probable that the pink discs are due to hydrogen, and that the grey discs indicate carbon. The tube contains nothing but hydrogen, mercury, and a minute trace of carbon; but with all the resources at my command I have not been able to get hydrogen quite free from impurity. Indeed I do not think absolutely pure hydrogen has ever yet been obtained in a vacuum-tube. I have so far succeeded as to completely eliminate the mercury, and almost completely to remove the trace of carbon.

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IX. *Notes on some Recent Determinations of Molecular Refraction and Dispersion.* By J. H. GLADSTONE, D.Sc., F.R.S.\*

AMONG the various indices of refraction which have been published by different observers of late years, there are some which have led me to further studies bearing on the general relation of this branch of Physics to Chemical theory. The following notes relate to the new metallic carbonyls, the metals indium and gallium, sulphur, and to liquefied oxygen, nitrous oxide, and ethylene.

I. METALLIC CARBONYLS.

Messrs. Ludwig Mond and Nasini† determined the molecular refraction of nickel tetracarbonyl for the red ray of

\* Read February 10, 1893.

† *Lincei, Rendiconti*, vii. 411.

hydrogen ( $H_a$ ) as 57·7, and the specific dispersion between the lines  $\gamma$  and  $a$  of hydrogen as 0·03475, which will give a molecular dispersion between those limits of 5·93. This indicates a very great refraction and an enormous dispersion.

Through the kindness of Mr. Mond I have been able to determine the refraction of two specimens of iron pentacarbonyl for several lines of the spectrum, with the following result. The second and third lines in the Table relate to the same specimen, the latter representing measurements taken in a very acute-angled prism, and under the most favourable circumstances for seeing the more refractive rays; nevertheless the spectrum was cut off so suddenly about the bundle of rays at G that I cannot be sure of the exact measurement, but think it differs little from the line  $\gamma$  of hydrogen.

Specimen.	Temp. C.	Sp. Gr.	$\mu_A$ .	$\mu_B$ .	$\mu_C$ .	$\mu_D$ .	$\mu_E$ .	$\mu_F$ .	$\mu_G$ .
I. ...	22°	1·460	1·5026	1·5076	1·5096	1·5180	1·5289		
II. ...	15·5	1·4705	1·5063	1·5117	1·5146	1·5224	1·5329		
II. ...	13·4	1·474	1·5071	...	...	1·5230	...	1·5446	1·5650

From these observations we obtain the following molecular refraction,  $\frac{\mu-1}{d}P=R$ .

Specimen.	$R_A$ .	$R_B$ .	$R_C$ .	$R_D$ .	$R_E$ .	$R_F$ .	$R_G$ .
I. ....	67·47	68·14	68·41	69·54	71·00		
II. ....	67·48	68·20	68·59	69·63	71·03		
II. ....	67·43	...	...	69·54	...	72·42	75·13

It is evident that in the iron compound also the refraction and dispersion are very great. The molecular refraction for the line  $a$  of hydrogen may be assumed at 68·5, and the

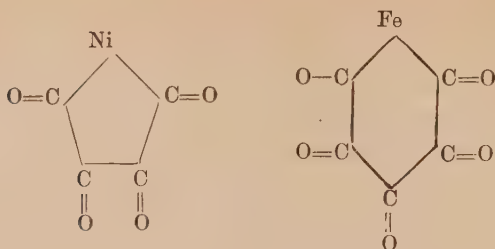


molecular dispersion between the lines  $\gamma$  and  $\alpha$  of hydrogen at 6.6. If we reckon for the lines A and H, we may assume H would be about 78.0, which would give a molecular dispersion between these limits of about 10.5.

In discussing their observations, Messrs. Mond and Nasini, assuming that CO has a molecular refraction of 8.4, reckoned the atomic refraction of nickel at 24.1, instead of 9.9, which I had assigned to this element in solutions of its salts, and which subsequently has been fairly corroborated by Nasini's own experiments. This difference they attributed to a difference of valency in the metal. By parity of reasoning the atomic refraction of iron for the line C would be 26.5, or 25.5 for the line A, instead of 11.6 previously determined for bivalent iron from solutions of its salts.

But this involves the assumption that CO in these carbonyls has the same value as we should expect to find in an organic substance. It also assumes that the nickel has 8 valencies, while the iron has 10, in the above-named compounds, and that iron has presumably  $\frac{7}{2}$  in diferrohepta-carbonyl; and that potassium in its compounds with CO has still other valencies. There is also another difficulty; for if we determine the atomic dispersion of nickel and iron on the same principle, it will be found to be 4.8 and 5.2 respectively for the interval between the lines  $\gamma$  and  $\alpha^*$ ; these numbers are about one fifth of the atomic refraction of the two metals given above, viz., 24.1 and 26.5. But the ratio between the atomic dispersion ( $\gamma - \alpha$ ) and the refraction of the most dispersive elements hitherto calculated, sulphur and phosphorus, is only about one tenth.

It seems more probable that the metals really retain their ordinary valency, and that the excessive refraction and dispersion is to be sought rather in the peculiar arrangement of the CO. In such compounds we may imagine the CO playing a part similar to that of the  $\text{CH}_2$  in ordinary organic compounds, which may be increased or diminished in number without altering the general type of the substance. In fact I accept on optical grounds as well as chemical, the ring-formulæ indicated in Mond's lecture at the Royal Institution.



In that case the molecular refraction due to each CO would be, from the nickel compound about 11·9, and from the iron compound about 11·3.

Although the atomic dispersion of nickel or of iron has not yet been definitely measured, it cannot greatly exceed 0·5 for  $\gamma - a$ . It is evident therefore from the figures for the dispersion, viz.,  $\text{Ni}(\text{CO})_4 = 5\cdot9$ ,  $\text{Fe}(\text{CO})_5 = 6\cdot6$ , that the molecular dispersion of each CO must be about the same in these two compounds, viz. 1·3, or thereabouts.

## II. INDIUM AND GALLIUM.

In 1885 I calculated the atomic refraction of indium and gallium from determinations of the refraction of certain alums made by M. Charles Soret. Very shortly afterwards he published another paper giving fresh and additional values for alums containing these metals\*.

For indium the available data are derived from rubidium and cæsium indium alums, and for gallium from no fewer than five compounds, viz., potassium, rubidium, cæsium, thallium, and ammonium gallium alums. Calculated from these data, I find as mean values for the atomic refraction of these two metals the following:—

Metal.	Atomic Weight.	Specific Refraction.	$R_A$ .
Indium .....	113·4	0·121	13·7
Gallium.....	69·9	0·166	11·6

\* *Archives Sc. Ph. & N. Genève*, xiv. p. 96.

These no doubt are nearer the truth than the higher figures previously given, though they must still be looked upon as only approximate. In regard to the atomic dispersion of these metals, the new observations quite confirm the previous remark that the order is "iron far the highest, chromium, indium, gallium, and aluminium lowest."

### III. SULPHUR.

In the following Table is given the atomic refraction of sulphur, either uncombined, or in very simple combination:—

Condition.	A.	C, or "red."	D, or "white."	F.	G or $\gamma$ .	H.
Solid .....	.....	15.7	16.0			
Liquid .....	15.98	.....	16.47			
Gaseous .....		16.1	.....			
In solution .....	15.5	15.7	16.0	16.7	17.3	
From CS <sub>2</sub> .....	15.8	16.05	16.3	17.05	17.7	18.4
" Cl <sub>2</sub> S .....	.....	15.8	16.0			
" Cl <sub>2</sub> S <sub>2</sub> .....	.....	15.9	16.1			
" Br <sub>2</sub> S <sub>2</sub> .....	.....	16.35	.....			

Sulphur in the solid condition is deduced from the observations of Descloiseaux and other physicists; but as the crystals of sulphur give three different indices of refraction for the same ray, the arithmetical mean of these three indices has been simply taken as the basis of calculation.

Sulphur in a liquid condition is from the observations of myself and the late Pelham Dale. It agrees, as far as D is concerned, with a determination by Becquerel.  $R_E = 16.86$ .

Sulphur in the gaseous condition was determined by Le Roux in 1861. The specific refraction was calculated out by me shortly afterwards, and recently by Nasini and Costa\*. I give their number for the atomic refraction in the Table.

The sulphur in solution is from five determinations of this element dissolved in carbon bisulphide which I made some years ago with another object, and which have never been published. The solutions contained from about 22 to 27

\* *Universita Inst. Ch. Roma*, 1891.

per cent. of sulphur. Two determinations of somewhat weaker solutions were lately published by Nasini and Costa, and were practically identical with mine. The refraction of 17·3 for the line  $\gamma$  is deduced from their figures alone.

The four last lines give the values of sulphur reckoned from its simplest compounds.

In the case of bisulphide of carbon the figures in the Table are derived from my own most recent observations, which agree closely with those of other observers. The deduction made for the atom of carbon is 5·0 for the line A, 5·26 for the line H, and proportional numbers for the intermediate lines.

In the case of bichloride of sulphur the calculations have been made from the observations of Costa; and in that of chloride of sulphur from those of Haagen, Becquerel, and Costa, which fairly agree. The refraction due to an atom of chlorine is assumed to be 9·95 for the line C, and 10·05 for the line D. Costa, in treating of these substances, has adopted a slightly smaller value for chlorine.

In the case of the bromine compound the sulphur is calculated from Becquerel's observations, taking the value for bromine at 15·35.

The figures for sulphur derived from these various sources are very similar. I doubt, however, whether the sulphur dissolved in bisulphide of carbon and the sulphur which forms part of that compound do exert exactly the same influence upon the rays of light. If we were to reckon the value of carbon in bisulphide of carbon by deducting the value found for sulphur in solution, we should get for A,  $36\cdot6 - 31\cdot0 = 5\cdot6$ , a higher figure than we ever find for carbon in a saturated compound. The difference would be still greater if reckoned by Lorenz's formula.

The accordance of the dispersion as exhibited throughout the Table is worthy of notice.

From the elaborate paper of Nasini and Costa, already referred to, it would appear that in some organic compounds, such as the xanthates, sulphur has at least the value of 16·0; but in the large majority of cases it has a distinctly lower value. In its oxygen compounds it is known to be far less refractive and dispersive.

## IV. LIQUEFIED OXYGEN, NITROUS OXIDE, AND ETHYLENE.

In the recent paper of Professors Liveing and Dewar (Phil. Mag., Aug. 1892) they give determinations of the specific refraction of liquefied oxygen, nitrous oxide, and ethylene. It is, of course, possible to compare these interesting results with what theory would have led us to expect. The authors have themselves done so in the case of liquid oxygen at its boiling-point of  $-182^{\circ}$  C. They remark that the refraction-equivalent, 3.182, which they found, differs but little from that deduced from gaseous oxygen at the ordinary temperature, viz. 3.0316, and "corresponds closely with the refraction-equivalent deduced by Landolt from the refractive indices of a number of organic compounds," which was 3.0. It actually comes between the two values, 2.8 and 3.4, which were assigned by Brühl to oxygen in its different states of combination with carbon, and to which an intermediate value has since been added.

Liveing and Dewar were able to determine the refraction of liquefied nitrous oxide for six different wave-lengths, the extremes being the red ray of lithium and G. These gave for  $\frac{\mu-1}{d}$  0.2595 and 0.2691 respectively, and for the molecular refraction of the red ray 11.418, and of G 11.840. The molecular dispersion between G and the lithium-line is therefore 0.422, which would indicate about 0.63 between H and A. Now it is difficult to say what the rational composition of nitrous oxide is, and therefore what its theoretical refraction and dispersion should be. Nitrogen in ammonia and its congeners is reckoned at 5.1, in nitriles at 4.1; oxygen double-bonded is reckoned at 3.4, with two separate bonds at 2.8. We therefore, according to our theoretical views, might reckon nitrous oxide at 13.6, 13.0, 11.6, or 11.0. The probability is therefore clearly in favour of the lower figure for nitrogen. As the dispersion-equivalent of nitrogen in ammonia is as high as 0.38, this would also seem to exclude the idea of the nitrogen in nitrous oxide being in the same condition as in ammonia. This will probably be considered the most likely alternative also on chemical grounds.



On calculating Messrs. Liveing and Dewar's numbers for liquid ethylene, we obtain the molecular refraction of 17·2 for the line D. But Professor Dewar has kindly furnished me with a more recent determination of what he believes to be a purer specimen. The refractive index, at the boiling-point, for the line C is 1·3445, and for the line F is 1·3528, the specific gravity being 0·55. These figures give 17·53 as the molecular refraction for the line C, and 17·92 for the line F. These will indicate about 17·41 for the line A. The theoretical value for ethylene, for the line A, is 17·4.

$$\begin{array}{rcl}
 \text{C}_2 & . & . & . & . & = 10\cdot0 \\
 \text{H}_4 & . & . & . & . & = 5\cdot2 \\
 \text{Double-linking} & . & . & . & & = 2\cdot2 \\
 & & & & & \hline
 & & & & & 17\cdot4
 \end{array}$$

The coincidence between experiment and theory is very striking.

PROCEEDINGS  
AT THE  
MEETINGS OF THE PHYSICAL SOCIETY  
OF LONDON.  
SESSION 1892-93.

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February 12th, 1892.

Prof. W. E. AYRTON, Past President, in the Chair.

Mr. W. R. BOWER and Mr. E. EDSEER were elected Members of the Society.

Professor S. P. THOMPSON, F.R.S., communicated a Note on Supplementary Colours.

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February 26th, 1892.

Prof. W. E. AYRTON, Past President, in the Chair.

The following communications were made :—

“On Modes of representing Electromotive Forces and Currents in Diagrams.” By Prof. S. P. THOMPSON, F.R.S.

“On the Flexure of Long Pillars under their own Weight.” By Prof. M. FITZGERALD.

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March 5th, 1892.

Prof. S. P. THOMPSON, Vice-President, in the Chair.

Miss L. E. WALTER was elected a Member of the Society.

The following communications were made :—

“Note on the Electromotive Forces of Gold and Platinum Cells.”

By Prof. E. F. HERROUN.

“A new Instrument for showing the effect of Persistence of Vision.” By E. STUART BRUCE, M.A.

“Some Electrical Instruments.” By Mr. R. W. PAUL.

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March 11th, 1892.

Prof. A. W. RÜCKER, Vice-President, in the Chair.

The following communications were made :—

“A Thermodynamic View of the Action of Light upon Silver Chloride.” By H. M. ELDER, M.A.

“On Choking Coils.” By Prof. J. PERRY, F.R.S.

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April 8th, 1892.

Dr. J. H. GLADSTONE, Past President, in the Chair.

Mr. C. T. MITCHELL, Barrister-at-Law, was elected a Member of the Society.

The following communications were made :—

“On the Construction of a Colour-Map.” By W. BAILY, M.A.

“A Mnemonic Table for changing from Electrostatic to Practical and C.G.S. Electromagnetic Units.” By W. GLEED, M.A.

“On the Law of Colour in relation to Chemical Constitution.” By Mr. W. ACKROYD.

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May 13th, 1892.

Dr. E. ATKINSON, Treasurer, in the Chair.

Mr. GERRANS was elected a Member of the Society.

The following communications were made :—

“An Instrument for describing Parabolas.” By Mr. R. INWARDS.

“Some Electrical Instruments.” By Mr. F. H. NALDER.

“A Portable Instrument for measuring Magnetic Fields.” By MESSRS. E. EDSER and H. STANSFIELD.

“On a Unit of Measurement of Light and Colour.” By Mr. J. W. LOVIBOND.

Mr. R. W. PAUL exhibited a form of Wheatstone Bridge.

May 27th, 1892.

Mr. WALTER BAILY, Vice-President, in the Chair.

A communication, “On the Present State of our Knowledge of the Connexion between Ether and Matter,” was made by Prof. O. J. LODGE, F.R.S.

June 10th, 1892.

Mr. WALTER BAILY, Vice-President, in the Chair.

The following communications were made :—

“On some Points connected with the Electromotive Force of Secondary Batteries.” By Dr. GLADSTONE, F.R.S., and Mr. HIBBERT.

“On Workshop Ballistic and other Shielded Galvanometers.” By Prof. W. E. AYRTON, F.R.S., and Mr. T. MATHER.

June 24th, 1892.

Prof. A. W. RÜCKER, Vice-President, in the Chair.

The following communications were made :—

“On Breath Figures.” By Mr. W. B. CROFT.

“On the Measurement of the Internal Resistance of Cells.” By Mr. E. WYTHE SMITH.

“On the Relation of the Dimensions of Physical Quantities to Directions in Space.” By Mr. W. WILLIAMS.

“On the Laws of Molecular Force.” By Mr. W. SUTHERLAND.

October 28th, 1892.

Dr. J. H. GLADSTONE, Past President, in the Chair.

Mr. G. H. WYATT was elected a Member of the Society.

Discussions took place upon Mr. WILLIAMS's paper "On the Relation of the Dimensions of Physical Quantities to Directions in Space," and upon Mr. SUTHERLAND's paper "On the Laws of Molecular Force;" in the course of which communications were made, "On the Determination of Critical Density," by Dr. YOUNG and Mr. THOMAS, "On the Determination of the Critical Volume" and "On the Boiling-points of Different Liquids at Equal Pressures," by Dr. YOUNG.

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November 11th, 1892.

Mr. WALTER BAILY, Vice-President, in the Chair.

Mr. PORTER was elected a Member of the Society.

The Discussion on Mr. WILLIAMS's paper "On the Relation of the Dimensions of Physical Quantities to Directions in Space" was continued.

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November 25th, 1892.

Prof. S. P. THOMPSON, Vice-President, in the Chair.

Messrs. T. G. FRY, A. G. BESSEMER, Junior, and E. F. FOURNIER D'ALBE were elected Members of the Society.

A communication on "Experiments in Electric and Magnetic Fields, constant and varying," was made by Messrs. E. C. RIMINGTON and WYTHE SMITH.

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December 9th, 1892.

Mr. WALTER BAILY, Vice-President, in the Chair.

Major H. E. RAWSON, R.E., was elected a Member of the Society.

The following communications were made :—

“On the Spectra of various Orders of Colours in Newton’s Scale.”

By W. B. CROFT, M.A.

“On the Diffusion of Light.” By Dr. W. E. SUMPNER.

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January 13th, 1893.

Prof. G. F. FITZGERALD, President, in the Chair.

Mr. HASELFOOT was elected a Member of the Society.

A communication on “Science-Teaching” was made by Mr. F. W. SANDERSON.

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January 27th, 1893.

Mr. WALTER BAILY, Vice-President, in the Chair.

Mr. T. W. MORTON was elected a Member of the Society.

The following communications were made :—

“On Japanese Magic Mirrors.” By Prof. S. P. THOMPSON.

“On the Functions of the Retina.” By Mr. W. F. STANLEY.

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*Annual General Meeting.*

February 10th, 1893.

Mr. WALTER BAILY, Vice-President, in the Chair.

The following Report of the Council was read by the Chairman :—

Since our last General Meeting there have been held fifteen ordinary business Meetings, in every case at the Laboratory of the Royal College of Science in South Kensington. As in the previous Report there was one, so now there are two more meetings to record than formerly was wont to be the case. This has been contrived by holding a meeting in October, though November has hitherto been the month for recommencing the meetings after the summer recess, and an extra meeting in January.

The Council has to mention the following deaths among the Members of the Society :—

The Rev. T. PELHAM DALE, M.A.; Mr. BENJAMIN LOEWY, F.R.A.S., one of the original Members of the Society; The DUKE OF MARLBOROUGH; Mr. C. E. WALDUCK; Mr. C. THOMPSON; Mr. P. W. WILLANS; Dr. HIRST; and on the 8th instant Mr. G. M. WHIPPLE, Member of our Council.

A new departure has been made which entails very much greater Secretarial work than heretofore. Most of our papers are now printed before being read, numerous proofs are sent to Members, and proofs and invitations are often sent to other scientific men who are likely to add, by their remarks, to the value of the discussions.

The numbers of the Society now amount to 371 Ordinary and 12 Honorary Members.

The following additions have been made to the Library during the year 1892-93 :—

*Newspapers and Magazines :—*

Nature.

The Electrical Review.

Engineering.

The Electrician.

Electrical Plant.

Ingeniero y Ferretero Español y Sud Americano.

Crónica Científica.  
 The Open Court.  
 Invention.  
 The Philosophical Magazine.  
 Beiblätter der Physik.  
 Annalen der Physik.  
 Journal de Physique.

*Journals of Societies, British:—*

Proceedings of the Royal Society.  
 Journal of the Society of Arts.  
 Journal of the Institute of Electrical Engineers.  
 Memoirs and Proceedings of the Manchester Literary and  
 Philosophical Society.  
 Quarterly Journal of the Royal Meteorological Society.  
 Proceedings of the Institute of Mechanical Engineers.  
 Proceedings of the Birmingham Philosophical Society.

*Journals of Societies, Colonial:—*

Geological and Natural History Survey of Canada.  
 Proceedings and Transactions of the Nova Scotian Institute of  
 Natural Science.  
 Hong Kong Observatory Observations.

*Journals of Societies, Foreign:—*

Proceedings of the Academy of Natural Sciences, Philadelphia.  
 Journal of the Physical and Chemical Society of Russia.  
 Mémoires and Séances of the Physical Society of France.  
 Journal of the College of Science of Japan.  
 Bulletin International de l'Académie des Sciences de Cracovie.

*Books, &c.:—*

North Atlantic Expedition. xxi.  
 Catalogue of Books added to Radcliffe Library, Oxford. 1891.  
 Sinopsis Mineralógica, by Carlos F. de Landero.

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The Rev. T. PELHAM DALE, M.A., was a son of the Rev. Thomas Dale, the well-known Canon of St. Paul's. He was born at Greenwich in 1821. He distinguished himself at Cambridge in the Mathematical Tripos, and became a Fellow of Sydney Sussex College. From 1847 to 1881 he was Rector of St. Vedast, Foster Lane, with St. Michael-le-Querne, in the City of London. In consequence of an action taken against him by his Churchwardens on a matter of ritual, he was committed to Holloway Prison for disobedience to the decision of the Court of Arches. On his release he retired to the quiet parish of Sansthorpe, in Lincolnshire, where he died last April. He was a man of varied attainments, and much interested in Mathematical and Physical Science. In early days he was occupied for a while in an engineer's workshop, and gave popular lectures and contributed to the 'Mechanics' Magazine.' In later life he was a Fellow of the Royal Astronomical Society, and served on its Council. About thirty-five years ago he took up the study of the Undulatory Theory of Light, and, in conjunction with Dr. Gladstone, he published several papers upon the subject of the Refraction of Light, two of which appeared in the 'Philosophical Transactions' for 1858 and 1863—one was on the "Influence of Temperature"; the other, "Researches on the Refraction, Dispersion, and Sensitiveness of Liquids." In later years he reverted to the subject in several papers communicated to this Society.

P. W. WILLANS, M.Inst.C.E., was killed suddenly on the 23rd May, 1892, at the age of 41, by being thrown from his carriage. Soon after his apprenticeship ended in 1874 he invented his famous high-speed steam-engine, and in the improvement and manufacture of his engines since that time he discovered for himself, and taught to mechanical engineers, many important matters in the application of thermodynamical principles; and there is a perfectly general acknowledgment among members of his profession that in doing this and in other ways his services to the steam-engine were as great as those of any man of this century. Electrical engineers in especial are under obligations to him.

Mr. Willans had excellences of ability and character rarely found united in one man. His perfect engineering training and clear-headed judgment enabled him to select and utilize whatever was valuable in the results of his long and costly thermodynamic researches. He will long be remembered for his courtesy and kind

heart. He was never so happy as when assisting others less gifted than himself.

Dr. THOMAS ARCHER HIRST, F.R.S., F.R.A.S., who died on the 16th February, 1892, at 7 Oxford and Cambridge Mansions, W., was born in 1830 at Heckmondwike, Yorkshire, and early in life made the acquaintance of Professor Tyndall, and acquired those tastes for mathematics, physics, and chemistry, which enabled him to occupy a distinguished position in the scientific world. He carried on studies in these subjects at Marburg, Hesse-Cassel, Göttingen, Berlin, and Paris, and during his career he held many appointments, and gave to the world a number of important writings on scientific subjects. In 1861 he was elected a Fellow of the Royal Society, and he was also one of the original Members of the London Mathematical Society, which was founded in 1864, under the presidentship of Professor De Morgan, by students of University College. He was a Member of its Council continuously from 1864 to 1883, was Treasurer for several years, and its President from 1872 and 1874. In 1865 Dr. Hirst was appointed Professor of Mathematical Physics in University College, London, which chair he held until 1867, when he succeeded De Morgan as Professor of Mathematics in that College. In 1870 he accepted the newly created appointment of Assistant Registrar in the University of London, in consequence of which he resigned not only his professorship, but shortly afterwards his general secretaryship of the British Association, an office he had filled since the meeting at Nottingham in 1866. Early in 1873, when the Royal Naval College was founded at Greenwich, he became director of studies, and held the post for ten years. Since his health obliged him to retire from his position at Greenwich, he has passed several winters abroad. He has, however, published since then several papers, which have appeared in the 'Proceedings' of the Mathematical Society of London. Dr. Hirst was three times a Member of the Council of the Royal Society, and twice one of its Vice-Presidents. In 1883 one of the Royal Medals was awarded to him. He was, too, a Fellow of the Royal Astronomical Society, an *ex officio* Member of the Council of the British Association for the Advancement of Science, an Honorary Member of the Naturforschende Gesellschaft at Marburg, of that of Halle, of the Société Philomatique, Paris, and of the Philosophical Society, Cambridge. He served for some years on the Council of University College, London, and in 1882 was made a Fellow of the University of London.



The death took place on the 8th of February, 1893, at his residence in Richmond, of Mr. GEORGE MATHEWS WHIPPLE, Superintendent of the Kew Observatory. Mr. Whipple had suffered from a painful internal complaint, but until a fortnight ago he was approaching convalescence, and his death was therefore unexpected. He was 50 years of age. He entered the Kew Observatory in 1858, and in 1862 became magnetic assistant. In 1866 the first set of results of sun-spot measurements was published, under the title of 'Researches on Solar Physics.' Most of the measurements were Mr. Whipple's, and subsequent editions of the work were under his direction. Mr. Whipple made a special study of wind-force and wind-velocities. He was, throughout the greater part of his life, constantly carrying on experiments with a view to determine wind-force, and to find out what were the best instruments for securing accuracy of results. In 1874 he made a series of experiments at the Crystal Palace, with the object of finding the constants of Robinson's anemometers; these were afterwards continued in another form, in conjunction with Mr. Dines. Mr. Whipple designed the apparatus used for testing the dark shades of sextants and other optical instruments; and also introduced several improvements in the Kew pattern magnetic instruments. In 1873 he was engaged with Captain Heaviside in making a series of pendulum-experiments to determine the force of gravity. In 1881 these experiments were repeated in association with Major Herschel, F.R.S., and in 1888 with General Walker, F.R.S. He contributed a number of important papers to the Royal Society. He was appointed Superintendent of Kew Observatory in 1876, and for the past 16 years he has also contributed results of investigations to the Royal Meteorological Society and to photographic publications. The magnetic part of the report of the Committee of the Royal Society which met to discuss the Krakatoa eruption and the subsequent phenomena were written by him.

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The adoption of the Report was proposed and passed unanimously.

The election of Officers and other Members of Council then took place, the new Council being constituted as follows :—

*President.*—Prof. A. W. RÜCKER, M.A., F.R.S.

*Vice-Presidents who have filled the Office of President.*—Dr. J. H. GLADSTONE, F.R.S.; Prof. G. C. FOSTER, F.R.S.; Prof. W. G. ADAMS,

M.A., F.R.S. ; The Lord KELVIN, D.C.L., LL.D., P.R.S. ; Prof. R. B. CLIFTON, M.A., F.R.S. ; Prof. A. W. REINOLD, M.A., F.R.S. ; Prof. W. E. AYRTON, F.R.S. ; Prof. G. F. FITZGERALD, M.A., F.R.S.

*Vice-Presidents.*—WALTER BAILY, M.A. ; Major-General E. R. FESTING, R.E., F.R.S. ; Prof. J. PERRY, D.Sc., F.R.S. ; Prof. S. P. THOMPSON, D.Sc., F.R.S.

*Secretaries.*—H. M. ELDER, M.A. ; T. H. BLAKESLEY, M.A., M.Inst.C.E.

*Treasurer.*—Dr. E. ATKINSON.

*Demonstrator and Librarian.*—C. VERNON BOYS, F.R.S.

*Other Members of Council.*—SHELFORD BIDWELL, M.A., LL.B., F.R.S. ; L. FLETCHER, M.A., F.R.S. ; Prof. G. FULLER ; Prof. O. HENRICI, Ph.D., F.R.S. ; Prof. J. V. JONES, M.A. ; Prof. G. M. MINCHIN, M.A. ; Rev. F. J. SMITH, M.A. ; W. E. SUMPNER, D.Sc. ; J. SWINBURNE ; JAMES WIMSHURST.

Votes of thanks were passed to the Lords Committee of the Council on Education ; to the OFFICERS ; and to the AUDITORS.

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THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM JANUARY 1ST, 1892, TO DECEMBER 31ST, 1892.

<i>Dr.</i>	£	s.	d.	<i>Cr.</i>	£	s.	d.
Balance in Bank, January 1, 1892.....			552 10 4	Balance due to Treasurer .....			£ s. d.
Entrance-Fees.....	19	0	0	Excess Subscriptions returned .....			1 0 0
Life Compositions .....	80	0	0	Taylor and Francis :—			0 6 0
Subscriptions for 1889 and before .....	13	0	0	Proceedings, vol. ii. (parts 2, 3, and 4).....	130	11	6
" 1890 .....	11	0	0	Physical Memoirs .....	2	6	6
" 1891 .....	28	0	0	Postage &c. of Proceedings.....	13	17	8
" 1892 .....	136	0	0	Members' separate copies.....	24	1	6
" 1893 .....	6	0	0	Miscellaneous printing.....	46	16	6
One year's Dividend on £400 Furness 4 per cent. De- benture Stock, less Income Tax .....		15	12 0				217 13 8
One year's Dividend on £200 Lancaster Corporation Stock, less Income Tax .....		7	16 0	Gyde (Binding) .....			4 4 3
One year's Dividend on £575 Midland 4 per cent. Pre- ference Stock, less Income Tax .....		22	8 6	Haggard (Binding).....			0 12 9
One year's Dividend on £200 Metropolitan Board of Works Stock, less Income Tax .....		6	16 8	Williams and Norgate (Periodicals).....			3 11 0
One year's Dividend on £251½ New South Wales 3½ per cent Stock, less Income Tax.....		8	13 6	Stationery.....			1 3 6
				Reporting .....			23 4 4
Sale of Proceedings, Books, and Memoirs.....				Attendance at Meetings and petty expenses .....			7 9 1
Balance due to Treasurer .....				Electric Light .....			0 11 6
				Purchase of £325 Midland 4 per cent. Perpetual Pre- ference Stock .....	431	18	3
				Less Dividend.....	6	6	9
							425 11 6
				Bank Charges .....			0 3 7
				Balance in Bank.....			266 13 10
				Petty Cash :—			
				Mr. Elder.....	4	10	1
				Mr. Blakesley .....	0	16	10
				Dr. Atkinson .....	1	5	3
							6 12 2
							<u>£958 17 2</u>

Audited and found correct,

HARRY M. ELDER,  
ALEXANDER PELHAM TROTTER, } *Auditors.*

February 4, 1893

# PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, DECEMBER 31, 1892.

ASSETS.		LIABILITIES.	
	£ s. d.		£ s. d.
Balance in Bank .....	266 13 10	Subscriptions in advance .....	6 0 0
Subscriptions due, estimated to produce .....	50 0 0		
£400 Furness 4 per cent. Debenture Stock .....	456 0 0		
£900 Midland 4 per cent. Preference Stock .....	1075 11 6		
£200 Metropolitan Board of Works Stock .....	217 0 0		
£200 Lancaster Corporation 4 per cent. Stock .....	224 0 0		
£254½ New South Wales 3½ per cent. Stock .....	249 7 5	Balance .....	2532 12 9
	<u>£2538 12 9</u>		<u>£2538 12 9</u>

Audited and found correct,

HARRY M. ELDER,  
ALEXANDER PELHAM TROTTER, } *Auditors.*

February 4, 1893.







